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X-Ray Diffraction Intensity of the Two Liquid Phases of Para-Azoxyanisol

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Further experiments with greatly improved conditions show that the liquid crystal swarms or groups of molecules at 125°C give an x-ray diffraction intensity distribution curve which is similar to but not exactly like that of the transparent liquid at 150°C. The former has a greater intensity at the peak, and a narrower peak with a steeper slope on the zero angle side. The group in the liquid crystal, about 10^6 molecules, does not have the same structure as the very much smaller and less stable cybotactic group in the liquid. The latter does not need to contain more than 25 to 50 molecules to account for the experimental evidence. The liquid crystal swarms may be descriptively regarded as a regimentation of modified cybotactic groups. A new temperature effect is strongly suggested by the apparent orientation of swarms in the liquid crystal with molecular axes perpendicular to the temperature gradient.

DIFFERENCES in experimental results for the x-ray diffraction intensity of liquid crystalline para-azoxyanisol, as reported by two observers,[1, 2] have rather required the additional experiments which are here reported. The question to be answered by experiment is: What is the change, if any, in the x-ray diffraction intensity in passing from the liquid crystalline to the transparent liquid state? An interpretation from the facts is of importance in a consideration of the difference between the two phases.

EXPERIMENTAL METHOD

The experimental method has been to place the sample in a thin-walled cylindrical blown glass tube having a diameter of 0.7 to 1.0 cm and a transmission of Mo $K\alpha$ radiation of approximately 80 percent. The orientation of the liquid crystal by the walls of the container would be effective for a distance not greater than 0.02 mm[3] and may be neglected. This container was placed in a cylindrical electric oven, internal diameter 7.3 cm, height 16.0 cm, with each of the two openings for the x-rays covered with two separated pieces of writing paper. The exit was kept small by attaching it to the rotating ionization chamber arm of the spectrometer. The apparatus was of the type described elsewhere,[4] spectrometer, methylbromide ionization chamber, zirconium and strontium filters for Mo $K\alpha$ radiation, but with the electrometer replaced by a vacuum tube amplifying circuit.[5] The specimen tube, 9 cm high, was enclosed in a cylindrical writing paper jacket. This prevented the air convection currents caused by oven circulation and produced a very steady temperature condition within. Two thermocouple junctions were

[1] G. W. Stewart, Phys. Rev. **38**, 931 (1931) and Trans. Faraday Soc. **29**, 982 (1933).
[2] W. Kast, Ann. d. Physik **19**, 571 (1934).
[3] Ornstein and Kast, Trans. Faraday Soc. **29**, 931 (1933).
[4] Stewart, J. Chem. Phys. **2**, 147 (1934), except that one of the Soller slits was 20 cm in length and the other 12 cm the dimensions of a single slit being 1.5×0.8 cm. A crystal diffraction curve showed a line width of 36″.
[5] An FP–54 (G.E. Co.) tube was employed with a balanced circuit as described by DuBridge and Brown, Rev. Sci. Inst. **4**, 532 (1935).

inserted through the jacket to within 2 mm of the wall of the tube and separated vertically by 1.5 cm, being within the level of the x-rays but not in the beam. A fan for vertical circulation was placed at the bottom of the oven. So effective was the surrounding paper cylinder that in practically all adjustments of temperature gradient at the tube, no change was produced by the operation of the fan. The presence of the paper made the production of temperature change in the liquid a very slow one indeed and it became necessary to wait at least three hours for a reasonably steady condition to be reached after the current in the heating coils was finally adjusted.

Experimental Results

In the case of the liquid phase the constancy of temperature was of no importance, for convection currents in the liquid did not alter the x-ray diffraction. On the other hand, as is well known, currents in the liquid crystalline phase do alter the orientation[6] of the liquid crystalline swarms or groups. The x-ray diffraction is very sensitive to this orientation as is shown by experiments[7] with an imposed magnetic field. In fact, it is just in the effect of convection currents that the difference between the results of the author and of Kast, referred to above, can be explained. With all the care exerted in the present experiment it is doubtful if convection currents in the liquid crystal were at any time entirely eliminated. As may be supposed, the absence of temperature gradient as shown by the thermocouples, together with the constancy of diffraction intensity, might be used to determine when the optimum nonconvection condition of the liquid crystal was obtained. Nonrotation of the glass container was necessary[8] because even a small constant rotation produced an alignment of liquid crystal groups or swarms. A reduction in peak intensity of 16 percent was produced by a rotation about the vertical axis of the container of 18 r.p.m. This effect corresponds

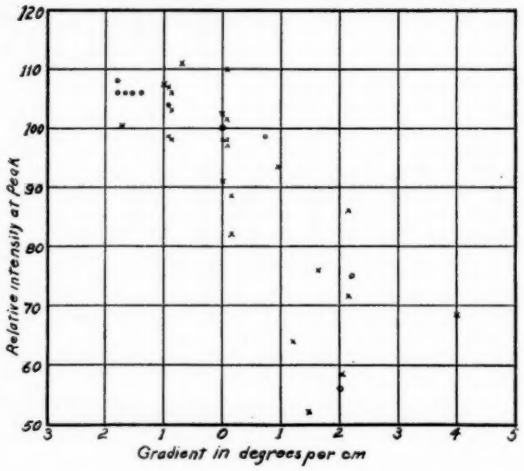

Fig. 1. Relative diffraction intensities at the primary maximum with varying temperature gradients in the liquid crystal.

to a preferential alignment of groups in a horizontal plane. Here it is inferred, as subsequently, that the longitudinal axis of a group or swarm in the liquid crystal is that which would be oriented in the direction of a magnetic field in the absence of thermal effects and that a group consists of molecules having axes parallel to each other and to the longitudinal axis of the group. This is in harmony with previous magnetic and convection experiments and the observations of the present report.

Effect of temperature gradient

The spectrometer angle, 2θ, for the maximum diffraction intensity of the liquid crystal is approximately 8.8°. The magnitude of this maximum, and also its exact angular location, depends upon the preference in orientation of molecules. As shown in magnetic results, if the molecular axes are vertical the diffraction in the horizontal plane is increased. Thus one might expect that with a temperature decreasing upward, convection would occur, increasing the magnitude of the intensity at the maximum. This is realized in practice by altering temperatures rapidly. This trend is also shown by Fig. 1. But the surprising result is that a temperature decrease downward, as shown in Fig. 1 is accompanied by a decrease in this intensity. The wide variation in position of points in Fig. 1 is caused by different conditions in the liquid at

[6] The orientation effect of flow upon oblong molecules has been known for a number of years (see Oseen, Trans. Faraday Soc. 29, 883 (1933). Such molecules in tubular flow are oriented with their axes parallel to the axis of the tubes.

[7] Stewart, Phys. Rev. 38, 931 (1931) and Trans. Faraday Soc. 29, 982 (1933) and others.

[8] The error from the inequality of the glass was negligible.

different times, for each one is an average of several measurements which differed among themselves by only 1 to 4 percent. The points are separated in time by at least several hours, and usually a day or more. The ones represented by circles were reduced to the same standard by assuming the value 100 zero temperature gradient. The remainder were adjusted assuming the transparent liquid to give a maximum of 85. On each occasion one or the other of these practically equivalent checks was employed. Apparently great care would not always produce the same intensity diffraction for the same temperature condition. This indicates that the same degree of preferred orientation, even randomness, could be only approximated and not obtained at will.[9] With reference to the depressed value of the maximum with the top at a higher temperature as shown in Fig. 1, an interpretation of the preference for horizontal orientation will later be discussed. For the moment attention is called to the fact that zero gradient may be accepted as a satisfactory condition of randomness of orientation, for it is at least the best obtainable. Throughout the work, the steadiness of the deflection with the transparent liquid as well as the apparent immunity from effect of a temperature gradient, caused one to accept the interpretation that, in the liquid phase, there was no preferential orientation in the body of liquid,

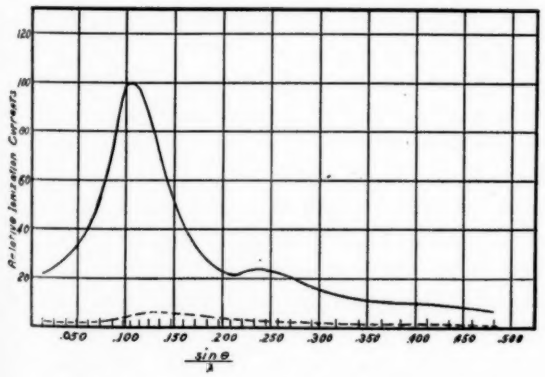

FIG. 2. Relative total intensity diffraction curve for the transparent liquid at approximately 150°C.

[9] Naturally the liquid crystal swarms are not all of the same size. Even the average size may not be independent of the direction of approach to a given temperature. Moreover Herrman (Zeits. f. Krist. **92**, 49 (1935)) has recently found differences in diffraction of certain liquid crystals which depends upon the direction in which temperature has changed.

0.2 cc in volume. Obviously the thermocouples just outside the thin-walled tube only approximated the temperature of the liquid on the interior, and this may be the cause in part of the irregularities in Fig. 1. But no interpretations are vitiated by this approximation.

Transparent liquid diffraction

In Fig. 2 is represented a mean curve for the transparent liquid at 150°C. Observations, not less than twelve, were made at each point indicated by the short vertical lines at zero ordinate. The maximum occurs at $(\sin\theta)/\lambda=0.105$ ($2\theta=8.55$) and minor peaks at $(\sin\theta)/\lambda=0.248$ and 0.420 ($2\theta=20.3$ and 34.6, respectively). 2θ is the diffraction angle read on the spectrometer. As indicated in the foregoing the diffracted intensity was always found to be independent of convection currents. The dotted curve is the effect of the glass container which has not been subtracted from the observed intensity.

In all the diffraction curves in this report corrections have been made for the stray radiation in the neighborhood of $2\theta=0°$, this being of noticeable magnitude from $2\theta=1°$ to 5° or 6°. Correction for absorption, incoherent radiation and shape of vessel are not necessary for the comparisons to be made of the two phases.

Liquid crystal diffraction

In Fig. 3 is represented a mean diffraction curve for the liquid crystal at 125°C. The maximum occurs at $(\sin\theta)/\lambda=0.109$ ($2\theta=8.84°$), a minor peak at $(\sin\theta)/\lambda=0.248$ and possibly another at 0.420. Fig. 3 was obtained by no less

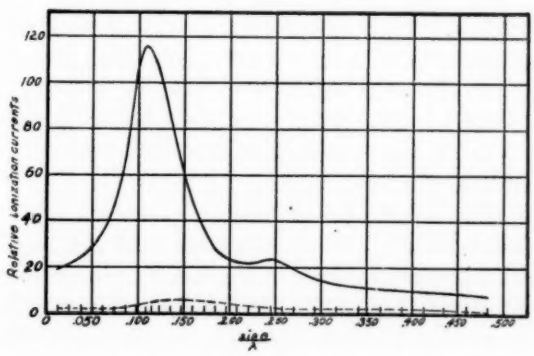

FIG. 3. Relative total intensity diffraction curve for the liquid crystal at approximately 125°C.

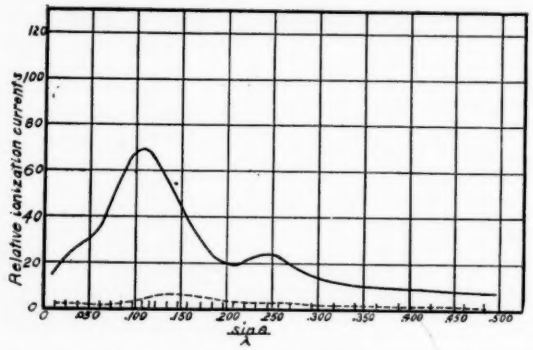

FIG. 4. Relative total intensity diffraction curve for the liquid crystal at approximately 125°C with a temperature gradient of 2.07°/cm, temperature increasing upward.

than five complete series over the entire range, each with four observations at angles indicated by the short vertical line on the zero coordinate. Also there were three additional partial checks at different times. In the five, one had a negative gradient (meaning higher temperature at the bottom) of 1.73°/cm, another of 1.00°/cm and the remaining three have less than 0.1°/cm. The degree of similarity of intensity of scattering at the peak angle in the five series, taken at different times is shown by the respective relative values 117.5, 113.5, 112, 113.5, 117.5 in the five complete series, and 117, 113 and 117.5 in the three partial checks. It is thought that even in these experiments where, for the most part, the temperature gradient is less than 0.1°/cm, there is a residue of convection currents which prevents random orientation of the swarms. This opinion arises from the fact that on three occasions a less intensity of the peak was observed, but in each of them the series was not regarded as satisfactory. Nevertheless the peak intensity was always greater than that with the transparent liquid and the peak was always narrower. Thus, the only error in adopting Fig. 3 as correct for the liquid crystal would be quantitative and not qualitative. The interpretations drawn would remain.

In Fig. 4 is shown the diffraction curve for the liquid crystal at a positive gradient of 2.07°/cm, the higher temperature at the top. The maximum is at $(\sin\theta)/\lambda = 1.082$ ($2\theta = 8.84°$), a minor peak at $(\sin\theta)\lambda = 0.248$ and possibly another at 0.420. Fig. 4 is not a mean, using varied conditions, but a measurement made on a single day with four observations at each angle used. It is presented to indicate a case of non-random orientation.

In Figs. 2, 3 and 4 the ordinate scales have been chosen so that the curves represent the correct relative experimental peak intensities.

Fluctuations in preferred orientation

The constancy of the galvanometer deflection for a given spectrometer angle was greatest with the liquid and least with the liquid crystal, the fluctuations in the latter being about twice those in the former. These fluctuations were noticeable from reading to reading, taken 10 sec. apart. In the liquid crystal phase there were also fluctuations of a longer time duration, sometimes 10 minutes in magnitude. The stability in the "depressed" state of liquid crystal was almost as good as that in the liquid phase.

Areas of diffraction curves

The areas under the curves plotted with relative intensities as ordinates but with the angle of the spectrometer, 2θ, as abscissae, varying from 0° to 40°, are as follows:

Fig. 2	55.2 liquid
Fig. 3	58.7 liquid crystal
Fig. 4	48.8 liquid crystal

It is assumed that the difference in interference effects in the two phases would be intermolecular and hence would occur within the angular range chosen. If the orientation of the molecular groups were, in all three cases, without a preferred direction, then the areas would be the same differences in density being disregarded. Difference in areas may be used as indicative of difference in preferred orientation, for the magnetic experiments with liquid crystals show that an alignment of swarms (and molecules) perpendicular to the incident x-ray beam, reduces the magnitude of the diffraction intensity or increases it depending upon whether this alignment is in the plane of the incident and diffracted beam or perpendicular thereto (or, in these experiments, horizontal or vertical). Assuming that, in the liquid phase, the cybotactic groups are without preferred orientation, then the comparison of areas and intensities shows that, in Fig. 3, the molecular swarms have a slightly preferred vertical orientation and in Fig. 4 a larger preferred horizontal orientation.

Width of diffraction peak

The width of the liquid crystal peak is less than that of the liquid. The width at 0.6 of the maximum height for Fig. 3 is 8 percent narrower for the liquid crystal than for the liquid in Fig. 2. In Fig. 4, with a distinct preferred horizontal orientation, the width is perhaps 20 percent greater.

Steepness of slope on inner side of diffraction peak

Measurements of the slopes of the curves at 0.6 the heights of peaks show that on the inner side this angle for the liquid crystal, Fig. 3, is 2 percent greater than for the liquid. This is also true for the additional measurements above mentioned in which the peak value was not so great. In the "depressed" liquid crystal curve, Fig. 4, the slope is approximately 14 percent less.

Temperature effect

The temperature difference, 25°C, and the corresponding change in density, 1.159 to 1.131[10] requires consideration in the comparison of the above diffraction curves. The ratio of the scattered intensities at any angle may be expressed as $I_1/I_2=(\rho_1/\rho_2)e$ exp $(\mu_2-\mu_1)t$ wherein I refers to intensities, ρ to densities, μ to the absorption coefficients, and the subscripts 1 and 2 to temperatures, 125°C and 150°C, respectively. Because the samples are at practically the optimum thickness for each, the correction for the difference in densities proves to be about 0.5 percent and is therefore omitted from consideration.

Position of diffraction peaks

The major peak values of $(\sin\theta)/\lambda$, liquid and liquid crystal, differ by three to four percent. It is believed that the accuracy of the location of the peaks is at least sufficient to negative any thought that the difference is caused by expansion. There is probably no significance in the differences in magnitudes of the two minor peaks in Figs. 2, 3 and 4, for the accuracy in the curve for the liquid was somewhat greater. These diffraction peaks at $(\sin\theta/\lambda=0.248$ and 0.420 are found in approximately the same positions as those in liquid benzene as shown by Katzoff[11] $(\sin\theta)/\lambda=0.255$ and 0.425 and by Wierl[12] using electron diffraction ($(\sin\theta)/\lambda=0.227$ and 0.421). One would anticipate that these minor peaks are caused by atomic arrangement in the benzene ring in the molecule of para-azoxyanisol.

Discussion

As already described, sufficient corrections have been made in the curves Figs. 2–4 to enable direct comparison to be made. The results are accurate enough to be used as a basis for the following interpretations and conclusions.

1. A general consideration of x-ray diffraction in liquids and of the constitution of liquid crystals, coupled with these and other x-ray diffraction experiments in para-azoxyanisol, leads to the conclusion that "structure" exists in both phases. In the liquid crystal it may be described as a swarm, consisting of about 10^5 or 10^6 molecules[13] with axes parallel and with mobility of the molecules within the swarm much less than in the very much smaller cybotactic groups in the liquid state.

2. A conclusion as to the exact relative scattered intensities at the diffraction-intensity-curve peaks of the liquid crystal and of the liquid, both with randomness of orientation of molecular groups, is not possible. The temperature conditions would lead one to claim Fig. 3 as representing this case for the liquid crystal. Here the peak intensity is 15 percent higher than that of the liquid. But both the greater area of the curve in Fig. 3 as compared with Fig. 2, and the occasional lesser intensity of the former found by experiment, lead one to conclude that the peak intensity with the liquid crystals in random orientation is greater than that with the liquid, the difference being of the order of five to fifteen percent. But one can say with certainty that the greater sharpness of the diffraction peak and steeper inner slope with the liquid crystal show more regularity of structure in that phase.

3. The differences in preferred orientation of the molecular grouping in the two phases, the liquid having no such preference, also indicates a difference in structure. In a liquid crystal, convection and temperature gradient (see below) cause orientation. The susceptibility in this

[10] Jaeger, Zeits. f. anorg. Chemie **101**, 152 (1917).
[11] Katzoff, J. Chem. Phys. **2**, 841 (1935).
[12] Wierl, Ann. d. Physik **8**, 521 (1931).
[13] For evidence for this value Ornstein and Kast, Trans. Faraday Soc. Discussion **29**, 931 (1935).

respect may be explained by the very great difference in magnitude of regions or groups in which noticeable orderliness or molecular arrangement occurs.

4. The depression and greater width of the depressed curve peak of the liquid crystal, and the discussion of areas are in harmony with the conclusion that a small temperature gradient produces a preferred orientation of the liquid crystal "swarms" or groups with their longitudinal axis perpendicular to the direction of the maximum temperature gradient. One hesitates to adopt this conclusion without reservation, for a detectable turning moment caused by the scattering of the elastic waves with such a small gradient seems surprising. The experiments were so carefully performed, however, that one may emphasize the striking agreement of this interpretation with the results of the numerous experiments reported in Fig. 1. Something certainly occurs that is, in our experiments, equivalent to this interpretation. At any rate these experiments may be regarded as adding confirmatory evidence to that from magnetic and electric studies, in emphasizing the relatively large size of these liquid crystal swarms.

5. The range of temperature in the liquid crystalline experiments would, with greater refinement, be of importance. The temperatures for the present observations varied from 122°C to 130°C without any noticeable effect on the location of the peak of the intensity diffraction curve or its magnitude. This does not mean that there can be no gradual alteration in structure in the liquid crystalline state, but only that it is small.

6. The size of the liquid crystalline groups must be quite large, as already stated. In the transparent liquid one has no definite measure of the size of the cybotactic groups. Experience in computation of diffraction intensity curves of liquids by using a density function leads one to expect that the size of the striking regularity in liquid groups of para-azoxyanisol would not need to be over 30A in its longer dimension with a gradual fading of regularity with distance. Thus one would anticipate no noticeable optical scattering. The large liquid crystal group is not merely an orderly aggregate of the small liquid groups for there is a definite change in structure. But the much larger aggregation of closely similar groups is a prominent characteristic of the change of phase.

I wish to acknowledge with thanks the research assistance of Dr. W. D. Phelps and Mr. B. J. Miller in the experiments herein recorded.

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X-Ray Diffraction Study of Liquid Sodium

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The x-ray scattering curve for liquid sodium is obtained photographically with Mo $K\alpha$ radiation, monochromatized by reflection from rocksalt. By a Fourier analysis of the corrected scattering curve, one obtains directly the radial distribution of atoms about any atom in the liquid. The distribution curve shows a first concentration at about 4.0A, followed by a dip at 5.0A, and a second concentration at about 7A. The significance of the curve as giving a picture of a simple monatomic liquid is discussed.

INTRODUCTION

IT has been shown[1,2] that from a Fourier analysis of the x-ray scattering curve of a liquid, one gets directly the radial distribution of atoms surrounding any average atom. It is of considerable interest to apply the method to a monatomic liquid, and get directly and uniquely a picture of this simplest type of liquid. Debye and Menke have successfully applied the method to liquid mercury. While mercury is an excellent example of a simple liquid, it is not however well suited to x-ray study, since the absorption co-

[1] Zernike and Prins, Zeits. f. Physik **41**, 184 (1927).
[2] Debye and Menke, Erg. d. tech. Röntgenkunde, II.

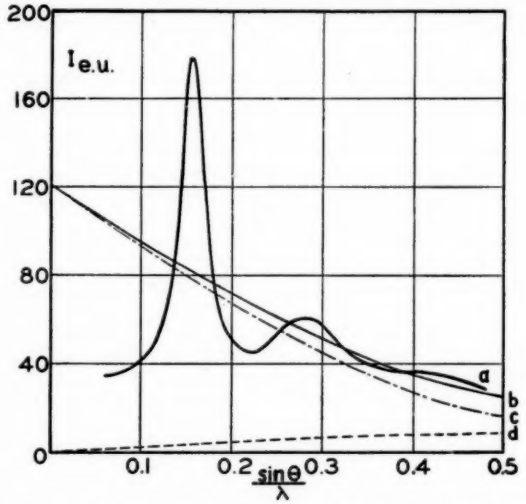

FIG. 1. (a) Corrected experimental intensity curve for liquid sodium in electron units per atom. (b) Total independent scattering per atom. (c) Independent unmodified scattering per atom. (d) Modified scattering per atom.

efficient for mercury is so large that the final intensity curve depends markedly upon the absorption correction. A better material for a quantitative x-ray study is liquid sodium. Using Mo $K\alpha$ radiation the absorption correction can be made practically negligible.

EXPERIMENTAL

The liquid sodium was contained in an evacuated thin-walled Pyrex tube[3] of diameter 2.0 mm, and maintained at a temperature of 103° by a heating coil. A test run showed that the scattering by the Pyrex tube was negligible compared to that of the sodium. The sample was at the center of a cylindrical camera of radius 8.61 cm. The radiation used was Mo $K\alpha$ monochromatized by reflection from a rocksalt crystal. At 35 kv and 20 ma exposures were of the order of 24 hours. The microphotometer record of the pattern was changed to an intensity curve in the usual way. The correction for absorption in the sample was negligible. Correcting for polarization, one obtains the final intensity curve in electron units on an arbitrary scale, Fig. 1a.

APPLICATION OF FOURIER METHOD

For a material containing only one kind of atom, the average density of surrounding atoms

[3] The technique of preparing the sample is described in Randall, *The Diffraction of X-Rays and Electrons by Amorphous Solids, Liquids and Gases*, p. 129.

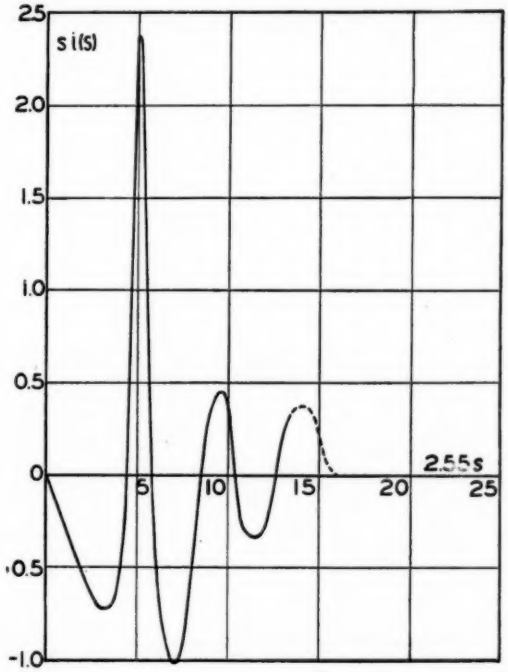

FIG. 2. The curve $si(s)$ for liquid sodium. The scale of abscissae $2.55s$ is chosen so that successive harmonics on the analyzer correspond to 0.4A intervals.

is given by the relation

$$4\pi r^2\rho(r) = 4\pi r^2\rho_0 + \left(\frac{2r}{\pi}\right)\int_0^\infty si(s)\,\sin rs\,ds \quad (1)$$

where

$4\pi r^2\rho(r)dr$ is the number of atoms between distances r and $r+dr$
ρ_0 = average density of sample in atoms per unit volume
$s = 4\pi \sin\theta/\lambda$
$i(s) = (I/N - f^2)/f^2$
I/N = unmodified intensity per atom in electron units
f = atomic scattering factor.

Curve 1c gives the independent unmodified scattering per atom f_{Na}^2, and curve 1d the modified scattering per sodium atom.[4] The total independent scattering per atom is given by curve 1b. At large values of $\sin\theta/\lambda$ the scattering curve of any material approaches independent scattering, and curve 1a is therefore drawn to such a scale that it approaches curve 1b at large values of

[4] From tables of f and Σf^2 Compton and Allison, *X-Rays in Theory and Experiment*.

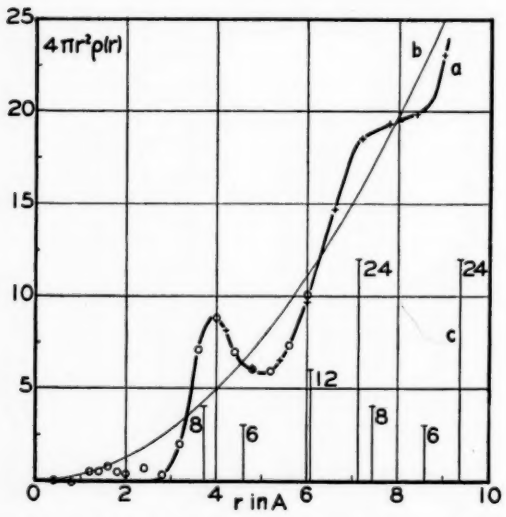

FIG. 3. (a) Radial distribution curve for liquid sodium $4\pi r^2\rho(r)$. (b) Average density curve $4\pi r^2\rho_0$. (c) Distribution of neighbors in crystalline sodium.

$\sin\theta/\lambda$. This serves to put the experimental curve upon an absolute basis, electron units per atom. Subtracting b from a, and dividing through by c, gives the quantity $i(s)$ in absolute units. On the experimental intensity curve, the outer part of the third peak is somewhat indefinite, and accordingly the outer part of the third peak on the $si(s)$ curve, Fig. 2, is arbitrarily rounded off. The integration involved in Eq. (1) is then carried out on a Coradi harmonic analyzer. By plotting the curve $si(s)$ to several different scales of abscissae, a large number of points are obtained upon the final distribution curve.

DISCUSSION OF RESULTS

The resulting radial density curve $4\pi r^2\rho(r)$ is shown in Fig. 3 plotted against r. The area under the curve in any region gives the number of atoms in that range of distances. The first concentration of neighboring atoms comes at about 4.0A. Beyond this point there is a slight dip, and then a second concentration at about 7A. At larger distance the density curve approaches curve b, the uniform density $4\pi r^2\rho_0$.

The resulting density curve is conveniently interpreted in terms of a box full of ball bearings continuously shaken. About any one ball bearing we will never expect to find another closer than the diameter of the balls. At about this distance we will expect to find the centers of several balls, since at any instant there will be a number of balls in approximate contact with the one under consideration. At a somewhat larger distance the number of centers must drop a little, since the balls already considered, prevent others from coming into the immediate vicinity of the first ball.

For purpose of comparison, the number of neighbors and their distances in crystalline sodium are also given in Fig. 3. It is very evident that the density curve of the liquid is essentially a smoothed out distribution curve for the crystalline phase. That this must approximately be the case, follows directly from the fact that the density of the liquid is not very different from that of the crystal.

The density curve of Fig. 3 represents the "structure" of liquid sodium as specifically as this quantity can be represented. It should perhaps be emphasized that this curve is obtained directly from the experimental x-ray curve, without making any *a priori* assumptions as to the atomic arrangement in the liquid. It is evident that there is such a thing as a "structure" in a liquid, a structure which has to do with the average distribution of neighboring atoms about any one atom. There appears to be no necessity for postulating a crystalline type of structure[5] in the liquid, to explain a distribution curve such as Fig. 3.

[5] By a *crystalline structure* one means an array of atoms in which some unit of structure repeats itself identically at regular intervals in three dimensions. In using terms such as "structure" it is necessary to state precisely whether *crystalline structure* is meant, or whether the term is being used in a more general sense.

Studies on the Decomposition of Azomethane

I. Description of the Apparatus*

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An apparatus for measuring the rates of gaseous reactions in the presence of large excesses of inert gases, using an adaptation of the Huygens manometer as the pressure measuring device, is described.

§1. INTRODUCTION

THE rate constant of a true unimolecular reaction tends to approach a constant value as the pressure is raised, but falls in value at low pressures, where the number of activating collisions is not sufficient to maintain the rate of reaction. Addition of an inert gas, which can exchange energy with the reacting molecule but which does not react chemically with it, may be expected to have the effect of increasing the rate constant by providing an additional source of activating collisions. Numerous experiments in which an inert gas has been added to a decomposing substance (usually an aldehyde or an ether) have been performed by Hinshelwood and his co-workers,[2] and they have invariably found that hydrogen apparently does have the anticipated activating effect. However, recent work has indicated that the decompositions which they have studied may be chain reactions,[3] and the interpretation of their work therefore becomes doubtful. In any event, these reactions are not as simple as they were once thought to be.[4] Others have reported similar work with nitrous oxide,[5] nitryl chloride,[6] and fluorine oxide[7] as the decomposing substances. There is no reason to believe that these decompositions involve chains, though the nitrous oxide decompositions is probably not a simple one.[8] Thus far, however, the only work on organic substances whose reactions probably do not involve chains is that of Nelles and Kistiakowsky[9] on the effect of hydrogen, nitrogen, propane, and carbon dioxide on the isomerization of dimethyl maleate, a reaction with very peculiar characteristics, and that of Ramsperger[10] on the decomposition of azomethane in the presence of nitrogen and ethane. It is the purpose of this series of papers to extend this work on azomethane, in order to get further information on the relative activating efficiencies of different gases, and because information on the azomethane decomposition itself may be obtained by studying it over a range of experimental conditions (see §9 of the following paper).

§2. DESCRIPTION OF THE APPARATUS

With pure azomethane it is possible to follow the course of the reaction at low pressures by measuring the increase in the pressure as the azomethane decomposes by means of a McLeod gauge, but the presence of an excess of inert gas precludes the effective use of this instrument. We have, therefore, made use of an adaptation of the Huygens manometer,[11] which enables one to

* Presented at the New York meeting of the American Chemical Society, April, 1935.

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[2] See, e.g., Hinshelwood, Proc. Roy. Soc. **A113**, 221 (1926); ibid. **A114**, 84 (1927); Hinshelwood and Askey, ibid. **A115**, 215 (1927); ibid. **A116**, 163 (1927); Glass and Hinshelwood, J. Chem. Soc., London 1804 (1929); Fletcher and Hinshelwood, Trans. Faraday Soc. **30**, 614 (1934).

[3] See (a) F. O. Rice and Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934); (b) Sickman and Allen, ibid. **56**, 1251 (1934); Allen and Sickman, ibid. **56**, 2031 (1934); (c) Leermakers, ibid. **56**, 1537, 1866 (1934).

[4] (a) O. K. Rice and Sickman, J. Am. Chem. Soc. **56**, 1444 (1934); (b) Fletcher and Hinshelwood, Proc. Roy. Soc. **A141**, 41 (1933).

[5] Volmer and Kummerow, Zeits. f. physik. Chemie **B10**, 414 (1930); Volmer and Froehlich, ibid. **B19**, 89 (1932); Volmer and Bogdan, ibid. **B21**, 257 (1933).

[6] Schumacher and Sprenger, Zeits. f. physik. Chemie **B12**, 115 (1931).

[7] Koblitz and Schumacher, Zeits. f. physik. Chemie **B25**, 283 (1934).

[8] Hunter, Proc. Roy. Soc. **A144**, 386 (1934).

[9] Nelles and Kistiakowsky, J. Am. Chem. Soc. **54**, 2208 (1932).

[10] Ramsperger, J. Phys. Chem. **34**, 669 (1930).

[11] Ostwald-Drucker, *Physiko-Chemische Messungen*, fifth edition (Akademische Verlagsgesellschaft, Leipzig, 1931), pp. 208, 210.

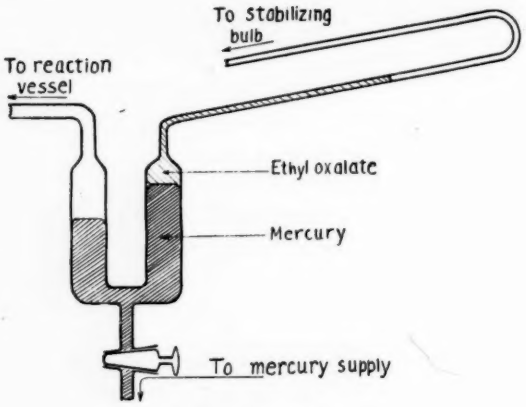

FIG. 1. Sketch of manometer.

measure very small changes in a large total pressure with an accuracy independent of the total pressure.

The reaction vessel (described in previous work[4a]) was a liter Pyrex flask immersed in a salt bath whose temperature could be controlled within 0.1°. The essential features of the Huygens manometer are shown schematically in Fig. 1. The sides of the U-tube were made of Pyrex tubing of 20 mm inside diameter and the height of the U-tube was somewhat over 70 mm. The U-tube contained mercury, the amount of which could be regulated, as it communicated through the stopcock shown with a mercury supply in a leveling bulb. On the surface of the mercury on the side which communicated with the reaction vessel were placed a few drops of a saturated solution of mercury di-*p*-tolyl (Eastman) in dibutyl phthalate as a lubricant.[12] While it might be thought undesirable to have such a solution in contact with the gas being studied, in actual practice there was no evidence of any appreciable error caused thereby, and as the measurements depended upon the reproducibility of very small movements of the mercury surface such a lubricant was absolutely essential. Diethyl oxalate was used as the light manometer liquid because it has a low viscosity and at the same time a fairly low vapor pressure.

It was necessary to thermostat the U-tube to within a few thousandths of a degree. There was, however, a length of perhaps eight centimeters of 2-mm tubing, extending through the bottom of the thermostat and the table on which it rested, between the U and the stopcock, which was not thermostated. This would not be of importance except in a slow run of long duration. In order to be able in such cases to check up on errors due to this or other causes an apparatus as nearly similar as possible to the one described was made and placed directly beside it, the reaction flask being in the same salt bath, the U-tube in the same water bath, etc. This duplicate apparatus could be used as a blank. The temperature of the ethyl oxalate in the slanting tube could be controlled sufficiently well by an air thermostat. To stabilize the system in case there should be some residual gas left in the ethyl oxalate after evacuation the end of the tube was connected, as indicated in Fig. 1, to a 500-cc bulb placed in the water bath.

[12] See Hickman, J. Opt. Soc. Am. **19**, 190 (1929); J. Phys. Chem. **34**, 650 (1930).

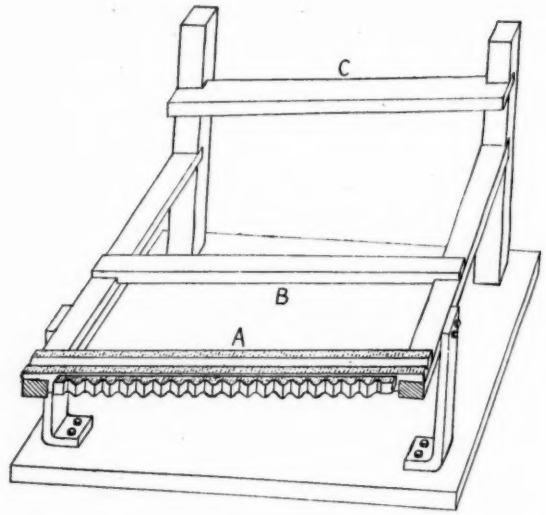

FIG. 2. Sketch of support for manometer tube. (The size of the teeth on the rack is highly exaggerated.)

The position of the ethyl oxalate meniscus was observed with a microscope mounted on a small brass platform which was in turn mounted on the metal frame sketched in Fig. 2. This frame had a rolled iron base, $9''\times13''\times\frac{1}{2}''$ which rested on three screws not shown in the diagram and was provided with a circular level so it could be placed so that it was exactly horizontal. The platform holding the microscope rested on the slanting brass cross-pieces *A* and *B*, being held firmly against them by a spring. Its motion along these pieces was controlled by a pinion which

meshed with the rack shown at the front of *A*, and was guided by the groove in *A*. The crosspiece *C* was used as a support for a specially ruled glass scale and for the slanting tube containing the ethyl oxalate meniscus which was firmly clamped to the frame and so held rigidly in position. The ethyl oxalate tube from the blank apparatus was just above the other one, and the microscope was mounted so that it could be focused on either one. A flash-light bulb attached to the microscope was used to illuminate scale and meniscus. A micrometer eyepiece was available for observing slow motions of the meniscus.

In using this apparatus the greater part of the pressure in the reaction vessel was balanced by the difference in height of the mercury on the two sides of the U-tube. The initial total pressure was measured by a McLeod gauge, which was then shut off from the reaction vessel. The small changes in pressure as the reaction proceeded were measured by observing the change in height of the ethyl oxalate meniscus. It was necessary, of course, to adjust the amount of mercury in the U-tube at the beginning of the reaction so that the ethyl oxalate meniscus would be on the scale. With some practice it was found possible to make a preliminary adjustment so that only a very small amount of mercury had to be added or removed after the gas was admitted to the reaction vessel. The final adjustment could usually be made and the readings begun within less than a minute after the reaction vessel was filled. Occasionally, however, the readings made during the next minute or two were irregular, this possibly being the time necessary for the mercury to come to final temperature equilibrium with the water bath.

It is obviously not possible to use such an apparatus for a very rapid reaction, and its usefulness also seemed to be limited rather more than we expected in the direction of very slow reactions, which confined us to mixtures in which the partial pressure of azomethane was about half a millimeter or greater. The measurement of the position of the meniscus was amply accurate for much lower pressures than that, but when the rate was very slow irregular changes in the position of the meniscus would occur. We believe that this could be eliminated by mounting the whole apparatus in a much more rigid fashion. Although the table on which the water bath rested was quite sturdy and the vacuum bench was strengthened with guy wires, a certain amount of vibration was possible, and by exerting pressure on parts of the vacuum bench it was possible to cause a motion of a millimeter or so in the position of the ethyl oxalate meniscus. The upper limit of total pressure which could be used with our apparatus was about 70 mm. The range in this direction could be increased by increasing the height of the U-tube (thus increasing the external volume, however) or by exerting a back pressure by means of an inert gas in the stabilization bulb. The limit to this method of increasing the range is set by the pressure which can be applied without driving the mercury into the horizontal part of the tube connecting the manometer to the reaction flask, and so depends on the length of the vertical part of the connecting tube.

A careful calibration of the apparatus was made by setting the ethyl oxalate meniscus at the lower end of the glass scale with the reaction flask evacuated, admitting a pressure of inert gas sufficient to move the meniscus to the other end of the scale and measuring the pressure by means of a McLeod gauge. This showed that 1 millimeter on the scale was equivalent to 0.0225 millimeter of mercury, within about two percent. The apparatus was also tested for readings on the intermediate part of the scale, taking intervals of about 30 mm (ethyl oxalate scale). These readings agreed with the over-all calibration within the accuracy attainable with the McLeod gauge (two to three percent). It is possible that the first 10 mm were off as much as five percent; however, this part of the scale was rarely used in practice. It should be noted that the calibration is made at very low pressures. At higher pressures a different part of the reaction vessel side of the U-tube is used. However, the U was so nearly uniform in diameter that any error due to this cause was negligible.

§3. Advantages of the Apparatus

The apparatus described has a number of advantages in addition to the possibility it affords of measuring reaction rates in the presence of large quantities of inert gases. It is possible with it to take many readings during the first five or ten percent of decomposition, even though that occurs within three or four minutes, and thus one is able to get a very good estimate of the initial rate of the reaction. Once the apparatus is set up it is very convenient to use. It is not in general possible to follow the rate of reaction through to the end without resetting the position of the ethyl oxalate meniscus, but if one is interested in the initial rate of reaction the runs can be made very quickly and easily. Some typical runs are presented in the following paper.

Acknowledgment

We are indebted to the Milton Fund of Harvard University for a grant which made possible the construction of this apparatus.

Studies on the Decomposition of Azomethane

II. Pure Azomethane and Azomethane in the Presence of Helium[1]

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(Received February 17, 1936)

In §§1–5 data on the decomposition of azomethane are presented and compared with those obtained by Ramsperger, with which they do not entirely agree. In §6 the possible effect of self-heating of the reacting gas is considered. In §7 some modifications in the theory of unimolecular reactions, called for if only partial deactivation occurs at collision, are discussed and found not to be of importance. The theory is applied to the present data and the pressure dependence of the rate seems to fit the theory better than was the case with Ramsperger's data. In §8 the effect of helium is discussed. It activates azomethane, being 0.120 as effective as azomethane itself. In §9 the possibility of the azomethane decomposition being a chain reaction is considered. It is concluded that if it is a chain reaction the chain is very short and its length is independent of temperature and pressure over the range studied in this research.

§1. Experimental Details

Preparation of materials

Several samples of azomethane were prepared by Thiele's[3] method, as used by Ramsperger[4] in his several researches and as described in detail by Allen and Rice.[5] The earlier of these were dried by passing the gas over calcium chloride and freed of air by distilling back and forth between dry ice traps; in the case of later samples the last trace of water was removed by distilling from a dry ice to a liquid-air trap, and air was removed by freezing out in liquid air and evacuating several times. No systematic differences were noted in the results obtained with the various samples.

The helium was taken from a tank obtained from the Ohio Chemical and Manufacturing Company and stated to be 96 percent pure. It was further purified by passing it in turn over hot copper (made from copper oxide by reduction with hydrogen), hot copper oxide, and fused potassium hydroxide. Mixtures of azomethane and helium were in all cases allowed to stand over night before using.

Experimental procedure

Runs were made at 290° and 330°C, the temperature being held within 0.2° of these values in practically all cases. In a few runs in which the temperature differed by perhaps 0.3° or 0.4° a small correction was made in the rate constant. The thermocouple was checked against a resistance thermometer several times during the course of the research. Variations of as much as 0.5° were noted, but this was within the accuracy of the resistance thermometer with the set-up available, and we have therefore used the thermocouple readings without correction. An error of 0.5° in the temperature would not be serious, in any event.

In making a run the gas was admitted to a one-liter flask, which was connected to the reaction vessel through a stopcock. To start the experiment the stopcock was opened, admitting the gas to the reaction vessel. After 15 seconds (20 seconds below 1 mm pressure) which was known by testing with inert gas to be sufficient time to allow pressure and temperature equilibrium to be established, the stopcock was closed. The remaining pressure in the outside bulb, measured with a McLeod gauge, was taken as the initial pressure. Measurements of the rate of change of pressure in the reaction vessel was then made by means of the Huygens manometer described in I.

In earlier runs at low pressures the blank, described in part I, was used to correct the readings of the Huygens manometer. In one case, in which the blank showed a very great variation, the run was discarded. In one case the correction introduced by the blank was ten percent, in one case five percent, in other cases still less. Since the correction appeared to be practically always within the error which is unavoidable at low pressures, this troublesome manipulation was omitted in later experiments.

§2. Experimental Results

In Table I we present the detailed data for two runs, which will illustrate the manner of using the Huygens manometer. Generally we made readings of the time (given in the second column) as the meniscus passed the successive millimeter marks on the glass scale back of the ethyl oxalate meniscus (readings given in the first column, Run 110). In column three is given the time required to pass from one millimeter mark to the next. In run No. 158 the first column of the table gives readings on the scale of the micrometer microscope with which the meniscus was observed and

[1] Presented in part at the New York meeting of the American Chemical Society, April, 1935. Part I, preceding paper.

[2] Present addresses: (a) University of California, Berkeley; (b) Columbia University.

[3] Thiele, Ber. **42**, 2575 (1909).

[4] Ramsperger, (a) J. Am. Chem. Soc. **49**, 912 (1927); (b) ibid. **49**, 1495 (1927). See also (c) J. Phys. Chem. **34**, 669 (1930).

[5] Allen and O. K. Rice, J. Am. Chem. Soc. **57**, 310 (1935).

TABLE I. *Data for some illustrative runs.*

RUN NO. 110 310°C; INIT. PRESS. AZOMETHANE, 6.52 mm			RUN NO. 158 290°C; TOTAL INIT. PRESS., 5.78 mm; INIT. PRESS. AZOMETHANE, 0.933 mm		
Manometer	Time (min.)	Δt	Micrometer	Time (min.)	Δt
31	2.23		7.5	1.83	
33	2.58	0.175×2	7.0	3.95	2.12
34	2.77	0.19	6.5	5.75	1.80
35	2.97	.20	6.0	7.78	2.03
36	3.17	.20	5.5	9.63	1.85
37	3.35	.18	5.0	11.45	1.82
38	3.53	.18	4.5	13.22	1.77
39	3.73	.20	4.0	15.00	1.78
40	3.93	.20	3.5	16.95	1.95
41	4.13	.20	3.0	18.68	1.73
42	4.33	.20	2.5	20.67	1.99
43	4.53	.20			
44	4.73	.20			
45	4.92	.19			
46	5.12	.20			
47	5.30	.18			
48	5.50	.20			
49	5.70	.20			
50	5.90	.20			

the third column gives the time required to pass from one entry of the first column to the next. The readings on the micrometer scale decrease as the pressure increases, and 2.5 divisions of the micrometer are equal to 1 millimeter on the glass scale, which in turn is equal to 0.0225 millimeters of mercury; in each case the zero of the pressure scale is arbitrary, depending on the setting of the instrument. The results presented in Table I will indicate the accuracy attainable with the Huygens manometer. In Table II and Fig. 1 we present a complete summary, giving the results in logarithmic form.

Table II includes all experiments made using the Huygens manometer with pure azomethane and azomethane in the presence of helium, except a few which were known to be spoiled, one run, noted above, discarded because of the blank, one in which there was a marked and continuous variation in the rate, and those made in a packed flask, which will be discussed below. In Fig. 1 No. 43, in which some gross error must have been made, is

TABLE II. *Summary of results.* (P_i=initial azomethane pressure, P_{He}=helium pressure).

PURE AZOMETHANE, 290°C			PURE AZOMETHANE, 310°C			HELIUM MIXTURES, 290°C				
RUN	LOG P_i (mm)	LOG ($K\times10^5$) (sec.$^{-1}$)	RUN	LOG P_i (mm)	LOG ($K\times10^5$) (sec.$^{-1}$)	P_{He}/P_i	RUN	LOG P_i (mm)	LOG ($K\times10^5$) (sec.$^{-1}$)	α (see §8)
15	1.395	1.098	23	1.261	1.673	4.96	48	0.981	0.986	0.03
1	1.388	1.040	38	1.140	1.631		49	.840	.957	.06
19	1.327	1.069	24	0.947	1.573		50	.681	.936	.12
6	1.239	1.055	108	.816	1.507		51	.561	.881	.10
11	1.202	1.035	110	.814	1.522		52	.415	.838	.11
9	1.202	1.025	109	.788	1.566		53	.279	.807	.15
357	1.083	0.933	39	.778	1.522		54	$\bar{1}$.947	.696	.19
16	1.076	1.003	355	.738	1.477		55	$\bar{1}$.812	.392	
2	1.061	0.969	58	.732	1.471	5.19	155	0.935	0.996	0.08
20	1.001	.991	67	.663	1.489		156	.609	.906	.10
7	0.919	.963	25	.635	1.459		157	.290	.792	.11
12	.885	.937	74	.538	1.411		158	$\bar{1}$.970	.650	.08
10	.881	.927	65	.527	1.365	9.83	159	0.723	0.983	0.11
154	.851	.908	221′	.527	1.434		160	.400	.871	.10
44	.774	.891	64	.525	1.365		161	.073	.760	.11
358	.762	.868	63	.523	1.363		162	$\bar{1}$.759	.609	.09
17	.756	.901	56	.520	1.386	HELIUM MIXTURES, 310°C				
3	.740	.865	66	.520	1.388	4.96	32	0.957	1.647	0.14
359	.698	.846	62	.515	1.371		33	.802	1.594	.14
21	.683	.895	40	.463	1.395		29	.681	1.537	.11
216	.618	.826	59	.420	1.345		34	.489	1.483	.14
8	.597	.848	356	.417	1.353		30	.356	1.433	.14
13	.554	.835	220′	.366	1.359		35	.172	1.351	.12
354	.533	.723	68	.351	1.337		36	$\bar{1}$.856	1.207	.11
45	.453	.781	26	.326	1.331		37	$\bar{1}$.544	1.120	.21
18	.437	.777	75	.225	1.269	9.82	163	0.728	1.651	0.20
4	.417	.757	72	.219	1.337		164	.411	1.505	.14
22	.368	.780	222′	.216	1.299		165	.097	1.438	.22
217	.262	.726	41	.152	1.228		166	$\bar{1}$.783	1.224	.10
14	.234	.688	60	.121	1.220	10.04	167	0.608	1.609	0.19
46	.137	.661	69	.044	1.194		168	.294	1.450	.11
5	.099	.595	27	.014	1.178		169	$\bar{1}$.975	1.306	.10
47	$\bar{1}$.822	.427	73	$\bar{1}$.910	1.304		170	$\bar{1}$.664	1.148	.08
			224	$\bar{1}$.907	1.110					
			76	$\bar{1}$.906	1.129					
			42	$\bar{1}$.863	1.107					
			61	$\bar{1}$.839	1.046					
			70	$\bar{1}$.744	1.099					
			43	$\bar{1}$.617	0.713					

also omitted. The runs tabulated in Table II represent data taken over the course of about a year. Runs 1 to 55 were made during July and August, 1934, runs 56 to 108 were made between November 26, 1934 and February 17, 1935, and runs from 154 between March 22 and July 30, 1935. Large gaps in the run numbers represent runs done in the presence of other gases, which will be presented later.

The rate constants, K, were calculated from the formula

$$K=(1n\ P_2-1n\ P_1)/(t_2-t_1), \qquad (1)$$

where P_1 and P_2 are the pressures of azomethane at times t_1 and t_2, respectively. In order to get the partial pressure of azomethane at any given time the readings on the Huygens manometer were first extrapolated back to zero time and the pressure in the reaction vessel at any given time then obtained by adding to the initial pressure the increase in pressure indicated by the Huygens manometer. The partial pressure of azomethane at any given time could then be found on the basis of the assumption that one molecule of azomethane decomposed to give exactly two molecules of products. This assumption may not be exactly correct, since the final-initial pressure ratio is greater than 2. However, it cannot make much difference as far as regards the relative rates of different runs, since in calculating the rate constants only the first part of a run was used; furthermore, since experiments on the decomposition of azomethane in the presence of ethane, to be reported later, indicate that azomethane probably reacts to some extent with the ethane formed in its decomposition, this seemed to be as reasonable an assumption as any for the first part of a run.

The pressure P_1 was calculated from a reading of the Huygens manometer taken early in the run, as soon as conditions had become steady, as indicated by the rate becoming essentially constant. Thus in run No. 110, Table I, P_1 was calculated from the reading of 33 on the Huygens manometer. Usually a shorter time was required for steady conditions to be attained than in this run. P_2 was calculated from the last reading taken on the manometer, except in runs which had proceeded too far toward completion, in which case it was calculated from a reading at an earlier point in the run, for example, from the reading of 39 in run No. 110, corresponding to about 7 percent decomposition. The runs at 290° were generally allowed to go to 3–5 percent of complete decomposition; for a few the calculations were made for somewhat greater completion. At 310° the calculations were generally made for 7–15 percent completion. In a few cases where the run had been allowed to proceed further toward completion calculations were also made (but not reported) on the basis of 20–25 percent completion. The differences were within the usual experimental error except perhaps for runs 63, 64, and 65, whose rate constants, as given in Table II do not agree well with the others, and which would in fact agree better if the constants for the longer period were used.

The rate constants calculated from Eq. (1) were finally corrected for external volume by multiplying by a, where $a=1+V_eT/VT_e$, the quantities V and V_e being the volumes of the parts of the reaction vessel and connecting tubing at the temperature, T, of the salt bath and the temperature, T_e, of the room, respectively. a varies, depending on the pressure, from about 0.04 to 0.07.

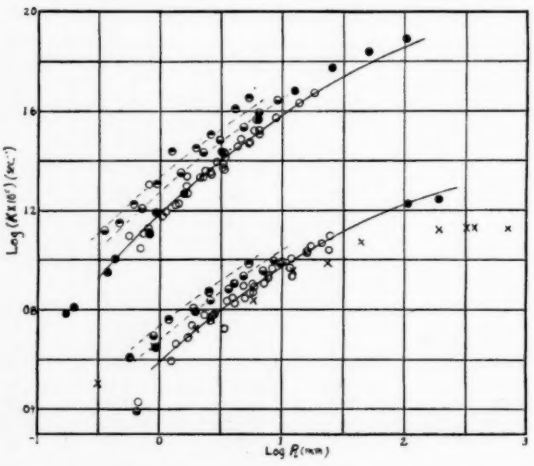

FIG. 1. Experimental results. Pure azomethane; Huygens manometer, open circles; McLeod, black circles; Ramsperger's results, ×. Azomethane with helium: Ratio of helium to azomethane pressure ~ 5, circles, lower half black; ~ 10, circles, upper half black. Curves are theoretical, upper for 310°C, lower for 290°C (see §7). Broken curves are for 5 : 1 and 10 : 1 helium mixtures ($\alpha=0.12$, see §8). P_i always refers to initial partial pressure of azomethane.

§3. Runs With the McLeod Gauge

For purposes of comparison a number of runs were made using the McLeod gauge (or, at high pressures, an ordinary mercury manometer) to measure the pressure changes. In these cases, since it was not possible to make enough readings during the first 10 percent of a run, they had to be carried further. This makes desirable a more careful correction for the external volume; according to Allen[6] the rate constant at any instant during a run will be given by

$$K=a(P_i{}^aP^{-a}q-1)^{-1}d\ \ln\ P/dt, \qquad (2)$$

where P is the *total* pressure, P_i the initial pressure, a, as before, is equal to $1+V_eT/VT_e$, and q is the number of molecules of product formed by one molecule of reactant (assumed to be constant during a run). Calculations for a typical run, illustrating the trend during a run obtained with all the McLeod gauge experiments, are given in Table III. The column headed P gives the partial pressure of azomethane in arbitrary units; the second column gives the time at which the pressure was attained; the third column gives K, calculated for the interval using Eq. (2) without integration (the quantity $P_i{}^aP^{-a}q-1$ being given its average value for the interval) and taking $q=2.00$; the

[6] Allen, J. Am. Chem. Soc. **56**, 2053 (1934).

TABLE III. *Data and calculations for an illustrative run.*

RUN NO. 97 310°C; INIT. PRESS. AZOMETHANE, 25.7 mm			
P	t (min.)	$K_{2.00}$ (sec.$^{-1}$)	$K_{2.17}$ (sec.$^{-1}$)
126.3	0		
130.3	1	56.5×10^{-5}	
138.2	3	59.1	50.1×10^{-5}
149.1	6	59.5	49.6
158.7	9	58.7	48.0
175.3	15	59.4	47.0
182.9	18	64.7	49.4
189.5	21	63.4	47.0
195.1	24	60.5	43.7
200.1	27	59.6	41.6
204.8	30	63.0	42.6
209.2	33	67.1	43.7
213.5	36	73.8	45.7
216.8	39	64.5	38.2
227.5	50	74.6	39.3

fourth column gives K calculated for $q=2.17$. The first value in the P column is P_i, obtained by extrapolation, and the first value of K is therefore of no significance except as a check on this extrapolation. The "initial" values of K for the runs made with the McLeod gauge or the mercury manometer, taking $q=2$, are summarized in Table IV (which also includes a value of K, calculated in the same way, for one run, 220′, which was carried to completion on the Huygens manometer). These values are obtained by averaging the values of K (excluding the nonsignificant first value) for about the first 25 percent of the run. The final-initial pressure ratios P_f/P_i for some runs which were allowed to go for 20–24 hours (corrected for external volume following Allen[6]) are also given. It will be noted that these values are considerably larger than that found by Ramsperger for this ratio, namely 2.04. No certain explanation of this difference can be given.

The values of K from Table IV are included in Fig. 1. It is seen that, while the agreement at the lower pressures, and, as well as may be judged, at 290° is very good, results at the higher pressures at 310° (Runs 95 to 100, inc.) are perhaps 15 percent higher than the results obtained with the Huygens manometer. The reason for this discrepancy is not known. Some slight difference might result from the different method of calculation, as illustrated by No. 220′, in which the calculation was made both ways, but this could hardly cause an error of much more than two percent and would be the same for runs at all pressures. One possibility that suggests itself is that the Huygens manometer exhibits a lag in the case of rapid runs, on account of the viscous resistance to flow of the diethyl oxalate in the narrow manometer tube. It is possible, however, to calculate what the lag would be, and it is readily seen to be so small as to have a negligible effect. Also the inertial resistance of the mercury in the U-tube is completely negligible, and surface tension effects would surely be expected to be of more importance at low velocities. There thus appears to be no reason why the Huygens manometer should not give correct results, and in view of the greater number of runs made with the latter instrument, their generally excellent consistency, and the fact that the runs were made at various times during the research, we believe that they are to be preferred. It is worth noting that runs No. 95 to 100 were made one after another at approximately the same time, namely on January 17, 18, 19, and 20, 1935, no other runs having been made between December 13 and February 4. Instances of apparently erratic results occurring in bunches were not entirely lacking when using the Huygens manometer. Thus runs 62–66, all except the last of which had very low rate constants, were made on the same day. Runs 63 to 65 had not only the low rate constant, but the same rather peculiar trend of the rate during a run, including a temporary speeding up of about ten percent at a certain point in the run, which was not observed in other runs; No. 62 exhibited a similar speeding up at an earlier point in the run. Runs No. 354 and 357, done on the same day, are both low, in spite of the fact that 355 and 356, done between them at 310° instead of 290°, are normal, and 358 and 359 (though showing some rather unusual irregularities during the run) are very slightly slow. Thus, despite the most careful manipulation, errors do occasionally occur and may be particularly deceptive on account of their apparent regularity. We believe that enough runs have been made with the Huygens manometer to guard against this possibility. Unfortunately we first obtained the K's for the McLeod gauge runs from the initial slope; this we later found introduced errors which made the results appear to agree better with those done with the Huygens manometer than they actually do, but unfortunately this was not discovered till the apparatus was dismantled, so that further runs could not be made.

In Fig. 1 we show for comparison the results obtained by Ramsperger[4b] at 290°. It is seen his trend with pressure does not agree very well with ours. It is difficult to assign a reason for this discrepancy.

TABLE IV. *Summary of results obtained with McLeod gauge, etc.* (Runs 93 and 94 at 290°C all others 310°C.)

RUN NO.	LOG P_i (mm)	LOG $(K\times10^5)$ (sec.$^{-1}$)	P_f/P_i	RUN NO.	LOG P_i (mm)	LOG $(K\times10^5)$ (sec.$^{-1}$)	P_f/P_i
93	2.280	1.246	2.16	101	$\bar{1}$.199	1.265	
94	2.033	1.228	2.18	105	$\bar{1}$.961	1.190	
95	2.017	1.890	2.21	102	$\bar{1}$.919	1.104	
96	1.709	1.839		106	$\bar{1}$.636	1.004	
97	1.410	1.772	2.19	103	$\bar{1}$.572	0.949	
98	1.105	1.681		107	$\bar{1}$.297	.810	
99	0.803	1.567	2.10	104	$\bar{1}$.227	.785	
100	.501	1.438	2.10	220′	0.362	1.378	2.09

§4. THE TEMPERATURE COEFFICIENT

The apparent activation energy was calculated from the vertical distance at 100 mm pressure between the two curves shown in Fig. 1. This gives 47,700 calories per mole, considerably lower than Ramsperger's value[4a] of 51,200, which is for approximately the same pressure. We would agree better with Ramsperger if we calculated the activation energy from the distance between the lower curve and the upper McLeod gauge points

rather to the upper curve. However, in view of the difference between our results and Ramsperger's at 290°, the discrepancy between 47,700 and 51,200 is not more than is to be expected.

If we use the curves of Fig. 1 to extrapolate to infinite pressure we get 50,200 for the true activation energy and $8\times10^{15}\exp(-50{,}200/RT)$ as the expression for the rate of reaction, as contrasted to $3\times10^{16}\exp(-52{,}400/RT)$ calculated by Kassel[7] from Ramsperger's results. The reason that the discrepancy at infinite pressure is less than that at 100 mm is to be found in the fact that our results indicate that we are not as close to the high pressure value as would be inferred from Ramsperger's results.

It is obvious that new measurements at higher pressures and over a greater range of temperature are greatly to be desired. This is true, not only to get a better test of the Rice-Ramsperger-Kassel theory,[8] but also because of the theoretical interest attaching to the absolute rate constant and the energy of activation.[9]

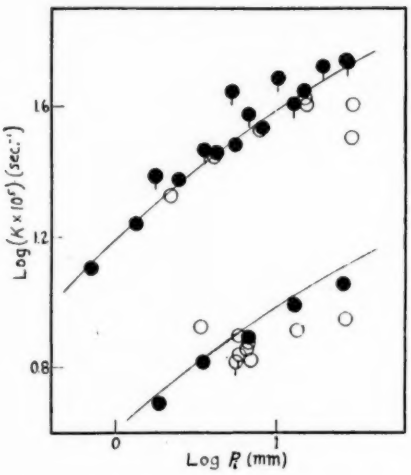

FIG. 2. Azomethane in packed flask. *First packing, open circles.* At 290.4°C, runs 345–351, open circles; runs 352–353, open circles with line. At 310°C, runs 360–365 (incl. 364′), open circles. *Second packing, black circles.* At 290.4°C, runs 384–388, black circles. At 310°C, runs 366–373, black circles with line; runs 377–383 (incl. 381′), black circles. Curves as in Fig. 1, but lower curve corrected to 290.4°C.

§5. On the Homogeneity of the Reaction

It was assumed at the outset, on the basis of Ramsperger's work, that the reaction was homogeneous. Since, however, our results did not agree exactly with his, it was decided that it would be desirable to make some further test of the homogeneity of the reaction. So some packing was prepared of clean Pyrex tubing, the ends flamed. This was placed in a new flask, giving a surface about six times that of the original flask. The first runs made in this flask (Nos. 345–351) had a tendency to be slow and irregular. The packing was removed and placed in a new flask which was used for runs 352, 353 and 360–365. These results are shown in Fig. 2. (Run 348 was not included on account of great variation of rate during the run.) It will be seen that the results were quite irregular, though the last four runs made fall well on the curve, which might indicate that the surface had become seasoned. Some new packing was then prepared and placed in a new flask, which was used for the rest of the runs. Between runs No. 373 and 377 four runs were made in this flask with azomethane and ethylene. It is seen from Fig. 2 that the results obtained with this flask, while still somewhat irregular, agree fairly well with the results obtained in the plain flask. The two worst runs were the second and third made with this flask; it is probable that after these the surface had become seasoned.

It will be apparent from the above account that under some circumstances, at any rate, the azomethane decomposition is affected by the surface. There appears, however, to be no reason to believe that the effect can be sufficient appreciably to disturb the results in the unpacked flask. The fact that two different samples of Pyrex tubing gave somewhat different results indicates the futility of attempting to reproduce a surface exactly. But even if the surfaces used by us are not truly comparable with that of the unpacked flask, the very fact that the results in the unpacked flask agree fairly well with those in the last packed flask and are not very different from those in the other is evidence in favor of the validity of those obtained with the unpacked flask. Furthermore there seems to be some indica-

[7] Kassel, *Kinetics of Homogeneous Gas Reactions* (Chemical Catalog Co., 1932), p. 196.

[8] (a) O. K. Rice and Ramsperger, J. Am. Chem. Soc. **49**, 1617 (1927); (b) ibid. **50**, 617 (1928); (c) Kassel, J. Phys. Chem. **32**, 225 (1928).

[9] O. K. Rice and Gershinowitz, J. Chem. Phys. **3**, 487 (1935).

tion that the surface becomes more inert after it has been used a while.

§6. Effect of Self-Heating of the Reacting Gas

The decomposition of azomethane is strongly exothermic. Thus the reacting gas can heat itself up, which in turn causes it to decompose faster. Under certain conditions this can result in an explosion. These effects have been studied by Allen and Rice,[5] and from their results it is possible to make some estimate as to how much the temperature may be increased under the experimental conditions used by us and those used by Ramsperger. According to Allen and Rice the rate of change of the partial pressure of azomethane at any time during the course of the run is given by the equation

$$-d(P/P^*)/dt = eK_0T_s/T_s^*, \tag{3}$$

where e is the base of natural logarithms, K_0 is the value the rate constant would have at the temperature of the bath provided no self-heating of the gas occurred, T_s is the difference between the actual temperature of the gas in the flask and the temperature of the bath, P^* is the critical explosion pressure for the given bath temperature, and T_s^* is the value of T_s when $P=P^*$, according to the simple theory of Semenoff.[10] T_s/T_s^* is given as a function of P/P^* by the equation

$$(T_s/T_s^*)e^{1-T_s/T_s^*} = P/P^*. \tag{4}$$

The rate constant at any time during the run is given by

$$K = -\frac{dP/dt}{P} = -\frac{P^*}{P}\frac{d(P/P^*)}{dt} = K_0e\frac{T_s}{T_s^*}\frac{P^*}{P} \tag{5}$$

from (3). The expression on the right can be evaluated in terms of P/P^* from Eq. (4), and if we are interested in the initial value of K/K_0 we can get it by evaluating eT_sP^*/T_s^*P for the initial pressure. If we are interested in the average value of K over a run which goes to completion we can get it by integrating (5) from $P=P_i$ to $P=0$ (where P_i is the initial pressure) and dividing the result by P_i. In Table V we give the values of K_i/K_0 and K_{av}/K_0 as a function of P_i/P^*.

Table V. *Correction of rate constant for self-heating.*

P_i/P^*	K_i/K_0	K_{av}/K_0	P_i/P^*	K_i/K_0	K_{av}/K_0
0.0	1.000	1.000	0.5	1.264	1.109
.1	1.039	1.013	.6	1.347	1.140
.2	1.083	1.033	.7	1.456	1.177
.3	1.134	1.056	.8	1.605	1.218
.4	1.194	1.081	.9	1.840	1.271

P^* for a 200-cc flask may be estimated from the work of Allen and Rice. The making of this estimate is somewhat complicated by the fact that the rate constant is not independent of pressure. However, we are interested in a sufficiently narrow range of pressures around 100 mm so that this variation can be neglected. Somewhat more serious is the fact that the "constant," x, which gives the rate at which heat is removed from the vessel apparently depends upon the pressure if the latter is above about 100 mm. In this case, too, we shall assume x is actually constant; since the whole theory we use is really based on that supposition, and since the actual runs in which we shall be most interested were made at 100 mm pressure or less, we can justifiably compare the P_i of such a run with the hypothetical P^* obtained on the assumption x does not vary, even though P^* be greater than 100 mm. Estimated values for P^* are given in Table VI.[11] The values for a 1000-cc flask are especially rough estimates since Allen and Rice found that x varies also with the size of the flask.

Now our experimental results approximate to a determination of the initial value of the rate constant, K_i. In order to estimate K_0 from our experimental results we should determine P_i/P^* with the aid of Table VI and then divide our experimental value by the appropriate value of K_i/K_0 taken from Table V. The only runs which would be appreciably affected are Nos. 95 and 96 of Table IV; the rate of 95 might be lowered by about ten percent, that of 96 by about five percent. This brings them closer to the theoretical curve of Fig. 1, but takes them rather out of line with the other runs which were made at the same time, all of which have rather high values, as we have seen.

Table VI. *Estimated explosion limits.*

	P^* (mm)	
T°C	200-cc flask	1000-cc flask
330	257	
310	1000	400
290	4000	1600

We shall probably do best to consider Ramsperger's results as experimental values of K_{av}. The correction thus indicated will be a slight underestimate since the runs were not carried quite to completion. Ramsperger's experiments were all done in a 200-cc flask, but the three experiments, reported by Ramsperger in his first paper, which were made at 320°C or higher were done in a packed flask, which should make the self-heating negligible, and it is easily seen to be negligible for all other experiments reported in his first paper. This is not true, however, of the experiments at 330°C in his second paper. Let us consider, for example, No. 82, $P_i=143.6$ mm, $K_{av}=2.65\times10^{-3}$ sec.$^{-1}$, which is typical. A rough extrapolation from the experiments at 323.7° and 327.4° (both of which fall about equidistant from and very close to the line in Fig. 1 of his first paper) indicates that K_{av} should be about 2.45×10^{-3} sec.$^{-1}$. This is exceeded by the observed value by about eight percent, which, while not far outside the experimental error, is nevertheless of interest, for it is about

[10] Semenoff, Zeits f. Physik **48**, 571 (1928); Zeits f. physik. Chemie **B2**, 161 (1929); or see reference 5, Eq. (4).

[11] These values are estimated from the straight line of Fig. 2 of Allen and Rice. The slope of this line was based on Ramsperger's value of the energy of activation. Using the value obtained from our results would lower the estimated explosion limits and so increase the estimated amount of self-heating, but only slightly.

what would be expected from Tables V and VI. In his second paper Ramsperger performed experiments at temperatures which were actually above our estimated explosion limit. This can only be possible because the value of x increases very rapidly at high pressures. Just what the excess temperature in the flask may be in these cases is difficult to say, but if the correction becomes greater than that calculated for No. 82 the corrected log $K-\log P_i$ curve would show a maximum. If, on the other hand, we assume that the excess of temperature is the same for all runs above 100 mm, the results of Ramsperger will conform more closely to the theory than was found by Rice and Ramsperger. In view, however, of the discrepancy between our present results and those of Ramsperger, the significance of this is doubtful.

§7. Theoretical

We shall now consider the application of the theory of Rice and Ramsperger to the present results. Various modifications of the theory have been considered by Kassel[12] and by Rice,[13] and Kassel states[14] that he has tried still others; these modifications have extremely little effect on the shape of the curves giving log K as a function of log P_i. It has seemed to us, however, that it would be of interest to consider another possible modification in the theory, which may very likely be included among those Kassel says he has tried but which has never been presented in detail. The assumption has always been made, in the theories of unimolecular reactions, that when an activated molecule is deactivated it always loses enough energy so as to place it in an energy range where the molecules are not reacting at a rapid enough rate to deplete their Maxwell-Boltzmann quota; then the rate of production of these activated molecules may be set equal to the rate at which they would be deactivated under equilibrium conditions, i.e., if no reaction occurred. This is undoubtedly a bad assumption. If we assume that the activated molecules do not lose enough energy for this to occur, but instead an amount, $\Delta\epsilon$, which as an approximation we take to be a constant, then the necessary modifications in the theory can be easily made. The rate constant for any unimolecular reaction at any pressure may be written in the form

$$K=N^{-1}\int_{\epsilon_0}^{\infty}Z_\epsilon b_\epsilon d\epsilon, \tag{6}$$

where N is the total number of molecules per unit volume, $Z_\epsilon d\epsilon$ is the actual number present per unit volume which have energy between ϵ and $\epsilon+d\epsilon$, b_ϵ is the probability per unit time that a molecule with total energy ϵ will react, and where ϵ_0 is the least energy a molecule must have in order to be able to react. According to the theories of Rice and Ramsperger or Kassel Z_ϵ is given in terms of the *equilibrium* number (per unit energy range), NW_ϵ, of molecules with energy ϵ by the equation[15]

$$Z_\epsilon=aN^2W_\epsilon(aN+b_\epsilon)^{-1}, \tag{7}$$

where a is a constant from the kinetic theory of gases, giving the collision number.[16] If, however, the above theories need to be modified, and it is assumed that the molecules of energy ϵ are formed on collision from molecules of energy[17] $\epsilon-\Delta\epsilon$, and if, on account of depletion through reaction the latter molecules are not present in their equilibrium quota (i.e., if $Z_{\epsilon-\Delta\epsilon}$ is not substantially equal to $NW_{\epsilon-\Delta\epsilon}$) then the value of Z_ϵ must be corrected corrrespondingly, so that

$$Z_\epsilon=aN^2W_\epsilon(aN+b_\epsilon)^{-1}(Z_{\epsilon-\Delta\epsilon}/NW_{\epsilon-\Delta\epsilon}). \tag{8}$$

Eq. (8) permits the evaluation of Z_ϵ for any ϵ; if $\epsilon<\epsilon_0$ then, since these molecules do not react, $Z_\epsilon=NW_\epsilon$, and for $\epsilon\leq\epsilon_0+\Delta\epsilon$, Eq. (7) holds. Z_ϵ may thus be evaluated for ϵ between ϵ_0 and $\epsilon_0+\Delta\epsilon$. This then permits its evaluation, from (8) between $\epsilon_0+\Delta\epsilon$ and $\epsilon_0+2\Delta\epsilon$; then it can be evaluated for ϵ between $\epsilon_0+2\Delta\epsilon$ and $\epsilon_0+3\Delta\epsilon$, and so on.

The original calculations of Rice and Ramsperger[8b] on azomethane were available, and these have been corrected in the manner indicated above, using $\Delta\epsilon=1000$ calories per mole, this being a reasonable guess. Once again it was found that the curves giving log K as a function of log P_i were practically unaltered in shape. They were shifted along the log P_i axis by about 0.45; in other words, for a given molecular radius and given number of squared terms, the rate would fall off to a given fraction of its high pressure value at a pressure increased by 2.8 (=antilog 0.45) fold. (The change in molecular radius or

[12] Kassel, J. Phys. Chem. **32**, 1065 (1928).
[13] O. K. Rice, Proc. Nat. Acad. Sci. **14**, 113, 118 (1928).
[14] Kassel, reference 7, p. 106.
[15] See reference 8a, Eq. (7).
[16] Not to be confused with the a of §§2 and 3.
[17] By the principle of microscopic reversibility this is equivalent to the statement that molecules lose an amount of energy equal to $\Delta\epsilon$ on collision.

number of squared terms necessary to compensate for this would be comparatively negligible.) The theoretical curves shown in Fig. 1 are the curves which have been corrected. The very slight difference between the corrected and uncorrected curves seemed to be such as to make the former fit the data a trifle better. (The difference in calculated rate constant between the corrected and uncorrected curves would not exceed two or three percent over the range of Fig. 1. Since the original calculations were made for 330° and 290° the curve for 310° was obtained by interpolation.

The agreement between our data and the theory appears to be better than was the case with the data of Ramsperger, though it is possible that this appearance is in part due to the fact that we have data over a smaller range of temperature and pressure, and in part to the self-heating of the gas which, as seen above, must have occurred in some of Ramsperger's experiments. In any event, we believe that the present state of the matter may be fairly summarized by the statement that theory and experiment agree within the limit of experimental error.

§8. The Effect of Helium

The results to be expected when a unimolecular reaction takes place in the presence of an inert gas are as follows. Suppose that the pressure of the reacting gas is P, that the pressure of the inert gas is P', and that the relative efficiency in activation or deactivation of the inert gas as compared to the reacting gas is α. Then the effective pressure, P_e, is given by $P+\alpha P'$ and we have

$$P_e/P=1+\alpha P'/P. \qquad (9)$$

If P'/P is held constant over a series of runs a curve will be obtained on plotting log K against log P which is shifted horizontally from the curve with no inert gas by the constant amount log P_e/P, provided α is independent of pressure.

It is reasonable to expect α to be independent of pressure, at least if the explanation of unimolecular reactions implied in the Rice-Ramsperger-Kassel theories is correct and there are no complications, for example, of the type considered by Rice[18] and by Fletcher and Hinshelwood[19]—and there seems to be no reason to suppose that there are such complications in the azomethane case. According to these theories the quantity which determines the probability of reaction of a given activated molecule is the amount of energy it contains, and so the only cause for a difference in α for different pressures would be a dependence of the ratio of the deactivating efficiencies of the inert gas molecules and reacting gas molecules on the energy of the molecule with which they collide.[20] Such a dependence on energy would certainly not be expected to be very marked, and we can anticipate that it would have a negligible effect in producing a dependence of α on the pressure, since the energy of activation changes only relatively slightly with the pressure. Likewise α should be practically independent of temperature.

The value of α for individual runs has been found by determining P_e/P from the horizontal displacement of the point from the theoretical curve in Fig. 1. These values have been included in Table II. As expected α is constant, within the limits of error, which are necessarily rather large since a small error in the measurement of the rate produces a relatively great error in α.

The grand average of all the α's is 0.120. This gives the relative activating efficiency of helium and azomethane compared pressure for pressure.

It may be of interest to compare these results with the effect of helium on other decompositions. It is unfortunate that no results are available for organic decompositions which certainly do not involve chains. Hinshelwood[21] found that helium had no effect within the limit of experimental error on the rate of decomposition of diethyl ether and Hinshelwood and Askey[21] obtained a similar result for dimethyl ether, but it is not certain how significant these results are as far as the activating effect of helium is concerned. Volmer and his co-workers[22] found that helium activated and deactivated nitrous oxide, α being 1.0. In this case it was also possible to estimate the absolute efficiency per collision of nitrous oxide in activating or

[18] O. K. Rice, Zeits f. physik. Chemie **B7**, 226 (1930).

[19] Fletcher and Hinshelwood, Proc. Roy. Soc. **A141**, 41 (1933).

[20] This may be taken as including any effect caused by molecules of the inert gas removing a different amount of energy at collision than molecules of the reacting gas. Although it has not actually been proved that such a combination of two different $\Delta\epsilon$'s would leave the shape of the log $K-\log P_i$ curve unchanged, the calculations of §7 make it appear most probable.

[21] Part I, reference 2.

[22] Part I, reference 5.

deactivating itself; it was found that 1/190 of all collisions were apparently effective in deactivation. In the case of fluorine oxide Koblitz and Schumacher[23] concluded that every collision of an activated molecule of fluorine oxide with an unactivated one of the same kind resulted in deactivation and found that α for helium was 0.68. There does not seem to be much basis for a comparison of these results with those obtained in the present paper. Nitrous oxide and fluorine oxide should surely be more like each other than like an organic molecule, and the difference in their behavior indicates that there is not much reason for expecting any similarity between either of them and an organic molecule, as far as energy transfer at collision is concerned.

§9. Can the Azomethane Decomposition Be a Chain Reaction?

The azomethane decomposition still furnishes the best test of the Rice-Ramsperger-Kassel theory of unimolecular reactions. It is, therefore, of great importance to consider all the evidence bearing on the question whether it is a chain reaction, for if it is a chain reaction this might invalidate its use as a test of the theory. The mere fact that the pressure dependence of the rate seems to fit the theory is no sufficient criterion that it is a simple decomposition rather than a chain reaction. For, as F. O. Rice and Herzfeld[24] have shown, it is possible for a chain reaction to be apparently first order at high pressures and three-halves order at low pressures. There is thus a falling off of the first order rate constant at low pressures, and while the theoretical curve differs from that predicted by the Rice-Ramsperger-Kassel theories, it is not sufficiently different over the range of pressures in which azomethane has been studied to make the discrimination between these possibilities certain.

A study of the photochemical decomposition of azomethane, such as has recently been made by Forbes, Heidt, and Sickman,[25] can throw some light on this question, if one can assume that the initial step of the photochemical decomposition is the same as that of the thermal decomposition. If the products formed in this step (believed in this case to be methyl radicals and nitrogen—the methyl radicals being the possibly reactive products) can react further with the azomethane, the photochemical decomposition will be expected to have a positive temperature coefficient. At sufficiently low temperatures, where these subsequent reactions are negligible, the quantum yield should be 1, and as the temperature is raised it should gradually increase, provided the secondary processes become of importance at a temperature below that at which the thermal decomposition becomes so great that the photochemical reaction cannot be followed. Such a situation has been observed in the case of acetaldehyde.[26] The experiments of Forbes, Heidt, and Sickman are, unfortunately, not entirely conclusive. They found that while the quantum yield at room temperature was one at sufficiently low pressures, it became smaller at higher pressures on account of the deactivation by collision of the photochemically excited molecules. It was not possible to work at a pressure such that the quantum yield was one and yet practically all the incident light was absorbed. Thus, while they found that at 150 mm the apparent quantum yield was 30 percent greater at 260° than at room temperature, since only part of the incident light was absorbed and the total amount absorbed was calculated from the absorption coefficient, the apparent change in quantum yield might have been due to a change in the absorption coefficient, which has been measured only at room temperature. It thus does not seem possible to conclude much about the chain length in the thermal decomposition except that it is most probably less than two at the pressure used by Forbes, Heidt, and Sickman. Since the rate changes by a factor greater than 2 between 150 mm and 0.5 mm, it appears that the dependence of the rate on the pressure cannot be explained by assuming it to be due solely to a change in chain length.

The effect of helium on the decomposition of azomethane throws additional light on this question. Helium is an inert gas, which certainly would not be expected to enter into any reaction with azomethane, and it seems improbable that it would affect the chain length if the azomethane decomposition is actually a chain reaction. It is, of course, conceivable that the rate of chain-breaking depends upon the diffusion of some intermediate such as methyl radicals to the wall,

[23] Part I, reference 7.
[24] F. O. Rice and Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).
[25] Forbes, Heidt, and Sickman, J. Am. Chem. Soc. **57**, 1935 (1935).
[26] Leermakers, J. Am. Chem. Soc. **56**, 1537 (1934).

and that this diffusion is hindered by the helium, thus increasing the rate. The fact that the first packing we used lowered the rate in some of the runs might be considered as confirmation of this, but it is probable that the effect of packing is due to condensation of material on the surface,[27] as is indicated by the fact that the first packing became darker with use than the second packing, which gave more normal rates. In any event, if the chain length depended upon the number of collisions of a methyl radical with azomethane molecules before hitting the wall, it would rapidly approach 1 at low pressures; with a chain length less than 2 at 150 mm it would surely be reduced to practically 1 at pressures around 5 mm, and if the sole effect of the helium were to reduce the diffusion of methyls to the wall, one would not then expect the addition of 5 or 10 mm of helium to 1 mm of azomethane to have any effect; it does, however, have an appreciable effect, indicating, we believe, that the effect of the helium is actually due to activation. We believe that the constancy of α over a range of pressures and two temperatures is strong evidence in favor of the view that the azomethane decomposition is not a chain reaction, or at least that the chain length is independent of temperature and pressure over that range. The falling off of the rate constant at low pressures must then be caused by lack of activating collisions, and the reaction is a satisfactory one to use as a test for the theory.

[27] Compare Winkler and Hinshelwood, Proc. Roy. Soc. **A149**, 355 (1935).

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Reaction Products of Ethyl Alcohol and Sodium Hydroxide

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A study has been made of the products formed when sodium hydroxide and ethyl alcohol react in the absence of water. Evidence has been found which indicates a reaction in which sodium ethylate and water are produced. Three types of tests have been made to determine the amount of water formed. The copper acetylide method, a volumetric method, and a method involving infrared absorption measurements all indicate a reaction which goes from 75 to 100 percent toward completion.

ALTHOUGH ethyl alcohol is usually regarded as a neutral liquid like water, in certain types of reactions it can be shown to act as a weak acid and in still others as a weak base. Thus, when ethyl alcohol reacts with an active metal such as sodium or potassium, hydrogen is given off and a salt is formed which is readily hydrolyzed by water. When treated with strong acids, alcohol forms addition compounds, which in general are unstable at ordinary temperatures.[1]

Engel and Lescoeur[2] have reported the following reaction between alcohol and the alkali hydroxides at high temperatures in the absence of water:

$$C_2H_5OH+KOH\rightarrow C_2H_5OK+H_2O.$$

In this reaction the alcohol obviously acts as an ordinary acid. However, owing to the difficulties involved in making an analysis, Engel and Lescoeur were unable to make any quantitative measurement of the extent of the reaction. For the case of potassium hydroxide Engel reports that, after the alcoholic solution of the hydroxide has been prepared at room temperature, subsequent cooling causes the deposition of needle-like crystals. Although these crystals when dried decompose rapidly at 60°C, Engel believes that they have the composition of $C_2H_5OK\cdot C_2H_5OH$. The mechanism of this reaction is shown by the following equation:

$$KOH+2C_2H_5OH\rightarrow C_2H_5OK\cdot C_2H_5OH+H_2O.$$

[1] H. J. Lucas, *Organic Chemistry* (Am. Book Co. 1935), p. 123.

[2] M. Engel, Comptes rendus **103**, 156 (1886); H. Lescoeur, Comptes rendus **121**, 692 (1895).

The complex form of the ethylate probably decomposes rapidly at high temperatures into ordinary potassium ethylate and alcohol. No quantitative tests on these crystals were possible.

It was the purpose of this investigation to make a study of this reaction by means of the infrared absorption of the reaction products. In order to do this it was necessary to find some part of the composite spectrum which would change in a manner depending upon the amount of one of the products formed. The bands in the spectrum of a solution arise from two sources:

(1) from the molecules of the components of the solution and
(2) from interactions between the molecules of different kinds.

The range 4μ to 5μ was chosen as the region for the observation of spectral changes. Weniger[3] has shown that compounds containing the ethyl group do not have strong characteristic absorption within this range, and Grantham[4] has shown that the band characteristic of inorganic hydroxides appears at a different wave-length (2.30μ). Thus, the alcohol, the ethylate, and the hydroxide by themselves are incapable of producing intense absorption between 4μ and 5μ. Water[5] in the liquid state, on the other hand, has a very strong absorption band at 4.7μ, and Williams and Plyler[6] have shown that this band is present in water-alcohol mixtures and that its intensity is a measure of the water content of the mixture. This 4.7μ water band is suitable for use as a measure of the amount of water formed in the reaction to be studied, unless other bands arising from association appear in the same position.

As for the existence of associational bands near 4.7μ, previous studies of binary mixtures of the compounds involved have shown that no appreciable associational bands are to be found near this point. A broad band with maximum at 5.2μ is present in aqueous solutions of hydroxides, while alcoholic solutions of hydroxides have a small, sharp band at this same point.[7, 8] In water-alcohol mixtures[6] the interaction bands occur at wave-lengths far removed from 4.7μ. As for associational bands in which ethylate-alcohol interactions are involved, the general experience has been that the bands arising from association of such similar organic compounds are either very weak or appear at wave-lengths much longer than 4.7μ. Thus, on the assumption that there are no tertiary associational compounds producing absorption in the 4μ–5μ region, it was decided that the 4.7μ band could be used as a means of testing for water formed in the reaction.

The alcoholic solution of sodium hydroxide was prepared by dissolving 11.1 grams of previously dried NaOH (Baker's C.P.) in 100 cc of anhydrous ethyl alcohol. The alcohol had been dried over lime, distilled, then dried over anhydrous copper sulphate, distilled again, and finally distilled from metallic sodium. The resulting alcohol gave only a faint color when tested by the copper acetylide method of Weaver[9] and of Hartley and Raikes.[10] The NaOH was fused in the usual manner.

The mixture was heated for one hour under a reflux provided with glass stoppers and ground glass joints. All apparatus had been heated to remove surface moisture before the reagents were introduced. The system was protected with a $CaCl_2$ tube. After an hour a sample was drawn, cooled, and immediately examined for the 4.7μ water band.

The remaining portion was distilled from the apparatus and collected in a receiver protected from the air by a $CaCl_2$ tube. Ground glass joints were used throughout in the apparatus. The distillate was tested for water by the aforementioned method of Weaver and others. A dense precipitate of copper acetylide was produced, indicating that a considerable amount of water had been formed in the reaction. This result was checked by means of a volumetric method involving a reaction between the water produced and calcium carbide with the production of acetylene.

In measuring the infrared absorption of the solutions a large type Hilger spectrometer with a fluorite prism was used as a resolving instrument. The effective slit-width was 0.04μ at 4.5μ. The

[3] W. Weniger, Phys. Rev. **31**, 388 (1910).
[4] G. E. Grantham, Phys. Rev. **18**, 339 (1921).
[5] E. K. Plyler and C. J. Craven, J. Chem. Phys. **2**, 303 (1934).
[6] Dudley Williams and E. K. Plyler, J. Opt. Soc. Am. (in press).
[7] E. K. Plyler and Walter Gordy, J. Chem. Phys. **2**, 470 (1934).
[8] E. K. Plyler and Dudley Williams, J. Chem. Phys. **2**, 565 (1934).
[9] E. R. Weaver, J. Am. Chem. Soc. **36**, 2462 (1914).
[10] H. Hartley and H. R. Raikes, J. Chem. Soc. **127**, 524 (1925).

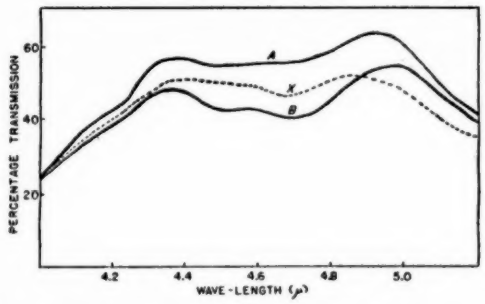

FIG. 1. The percentage transmission of absolute alcohol and two solutions. *A*, absolute alcohol, *B*, five percent water in alcohol. *X*, cell of unknown water content.

cell windows were of fluorite, and the cells were prepared by placing mica washers 0.05 mm in thickness between the fluorite plates. The fluorite plates, the mica washers, and all instruments used in preparing the cells were kept in a desiccator with P_2O_5 for several hours before being used. This minimized the possibility of difficulties arising from water adsorbed on the plates.

In Fig. 1 are shown the results obtained in the absorption measurements. Curve *A* represents the percentage transmission of the anhydrous alcohol used in preparing the solution. Curve *B* shows the transmission of a solution of five percent (by volume) of water in this same sample of anhydrous alcohol. It will be noted that near 4.7μ there appears a broad depression, which indicates the presence of water. The dotted curve *X* represents the results obtained with the solution of unknown water content. It will be noted that in general this dotted curve lies between the other two curves, showing that there is no strong characteristic absorption in this region arising from substances other than the water, which produces the broad depression near 4.7μ. Beyond 4.9μ, however, the curve *X* lies much deeper than the other two. This absorption arises from associations in which the remaining NaOH molecules are involved. The broadness of the 5.2μ band indicates that the solvation effect probably involves chiefly the NaOH and water rather than the NaOH and alcohol, since the NaOH-alcohol band is much narrower than this band. By a comparison of the intensities of the bands observed near 4.7μ it is estimated that the unknown solution probably contains from one-half to two-thirds as much water as the 95 percent solution. This calculation corresponds to a reaction which goes from 75 to 100 percent toward completion.

The results obtained in this study indicate the possibility of using infrared absorption measurements in still other cases where ordinary analytical methods are not readily applicable.

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The Structure of Ice III

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The stability of the high pressure ice forms discovered by Tammann and Bridgman at very low temperatures and atmospheric pressure has made it possible to obtain x-ray diffraction photographs of these forms. Since ice III is extracted from the press by taking it through the ice II region the precautions taken to avoid consequent misinterpretation of the ice III films are given. The analysis of the ice III diffraction patterns leads to a body-centered orthorhombic structure, and a unit cell of dimensions $a=10.20$A, $b=5.87$A, and $c=7.17$A. The unit cell contains sixteen molecules, has the symmetry of space group V_h^{26}-Ibam, and leads to a value for the density of 1.105 g per cc. Each oxygen ion is surrounded by a distorted tetrahedron of oxygen ions in a manner similar to that of ice I. An arrangement of the hydrogen atoms is proposed which makes the ice III lattice ionic. The volume decrease in the ice I–ice III transition is shown to be the result of a rearrangement of the oxygen ions. A simple transition mechanism is described, which is used to interpret some of the phenomena observed by Bridgman. The nature of the ice II–ice III transition is also discussed. A correlation between the latent heat of the solid-solid reactions involving ice I, ice II, ice III and the H−O−H bond angles is suggested. Some remarks are made concerning the liquid-solid reaction at high pressure. A brief description of some qualitative results obtained from the unanalyzed ice V and ice VI films is made. A summary of all the conclusions drawn from the high pressure ice investigations is made.

* Now at The United Drug Co., Boston.

Introduction

The existence of polymorphous ice forms at high pressures was first discovered by Tammann,[1] and was later thoroughly investigated by Bridgman[2] who discovered several additional forms. These forms are not stable at ordinary temperatures and atmospheric pressure, but can be kept indefinitely at atmospheric pressure if the temperature is maintained sufficiently low. This property has made it possible to take x-ray diffraction photographs of these forms, the analysis of one of which, ice II, has already been reported.[3] In this paper the structure of another of these polymorphous forms, ice III, is analyzed and its properties discussed.

Experimental Work

The range of pressure and temperature over which each ice form is stable is shown in Fig. 1, which is taken from Bridgman's original paper.[2]

The methods used to obtain diffraction photographs of the high pressure ice forms have been fully described elsewhere.[4] It will suffice here to say that the crystals were placed in a powder diffraction camera whose liquid air jacket kept the temperature of the crystals during exposure at −155°C.

It is evident from Fig. 1 that in order to get ice III out of the press it is necessary to pass through either the ice I or ice II regions at a relatively high temperature. A path through the ice II region was adopted as the most feasible method of extracting ice III from the press. This path was chosen because of Bridgman's observation[2] that if ice II had never been present in his system it was possible to sub-cool ice III at least −70°C with respect to ice II. Hence, in removing ice III from the press it was cooled as rapidly as possible through the ice II region before the pressure was lowered to atmospheric pressure. However, this traverse of the ice II region made it necessary to take precautions against possible traces of ice II on the ice III films. This was done by making two types of exposures,

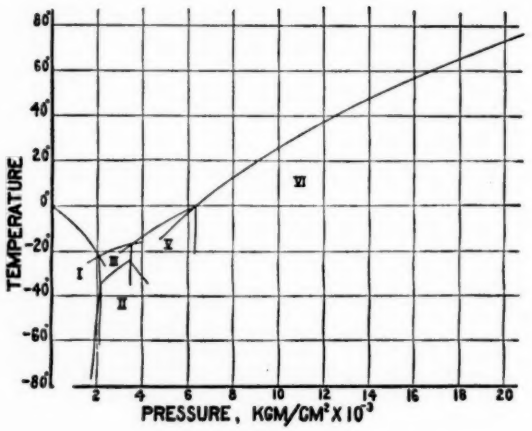

Fig. 1.

1. With the crystals untreated after leaving the press.
2. With the crystal first powdered by grinding under liquid air.

Invariably the first type of exposure gave a spotty type of pattern characteristic of a conglomerate of relatively large crystals. But in every ice II pattern ever obtained, and no ice II crystal was ground under liquid air, the lines were those of a perfect powder pattern irrespective of the path followed in the phase diagram, Fig. 1. Accordingly the spots appearing on the ice III films were taken as characteristic of the ice III crystal. Interplanar distances corresponding to these spots were obtained by superposing the ice III film on an ice I powder pattern, whose lines corresponded to known interplanar spacings. The relative intensities of the reflections corresponding to these spots were checked by visually estimating the intensities of the corresponding lines obtained from the ice III crystals powdered under liquid air. Various attempts were made to powder the ice III crystals by crossing the I–III and V–III phase lines. These attempts were not very successful, and in addition it was impossible to say with certainty that no ice I or ice V crystals were present as a result of incompleted reactions. All ice III crystals used in this experiment were made by putting 2500 atmospheres pressure on the liquid, and then lowering the temperature.

Just as for ice II, two different methods were used in estimating the density of ice III at atmospheric pressure from the Bridgman compressi-

[1] Tammann, *Kristallisieren und Schmelzen* (Barth, Leipzig, 1903), pp. 315–344.
[2] P. W. Bridgman, Proc. Am. Acad. **47**, No. 13 (1912).
[3] R. L. McFarlan, J. Chem. Phys. **4**, 60 (1936).
[4] R. L. McFarlan, Rev. Sci. Inst. **7**, 82 (1936).

bility data. In the first of these it was assumed that ice III would show the same relative change of volume over the pressure range 2100–1 atmospheres as does ice I. In the second method the ice III compressibility-pressure curve was extrapolated to one atmosphere, whence the density could be computed from the average compressibility. These methods yielded an average density of 1.105 gr per cc which is probably accurate to within ten percent.

The observed interplanar spacings are in excellent agreement with those to be expected from an orthorhombic cell where $a=10.20$A, $b=5.87$A, and $c=7.17$A, the axial ratios being $1.73:1:1.22$. Sixteen molecules per unit cell give a value for the density of ice III of 1.105, the exact agreement with the extrapolated Bridgman value being fortuitous. The observed intensities are in good agreement with those predicted by space group V_h^{26}-Ibam, where the coordinates of the oxygen atoms are

xyz	$x, y, \frac{1}{2}-z$	$x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2}$	$x+\frac{1}{2}, y+\frac{1}{2}, \bar{z}$
$x\bar{y}\bar{z}$	$x, \bar{y}, \frac{1}{2}+z$	$x+\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}-z$	$x+\frac{1}{2}, \frac{1}{2}-y, z$
$\bar{x}y\bar{z}$	$\bar{x}, y, \frac{1}{2}+z$	$\frac{1}{2}-x, y+\frac{1}{2}, \frac{1}{2}-z$	$\frac{1}{2}-x, y+\frac{1}{2}, z$
$\bar{x}\bar{y}z$	$\bar{x}, \bar{y}, \frac{1}{2}-z$	$\frac{1}{2}-x, \frac{1}{2}-y, z+\frac{1}{2}$	$\frac{1}{2}-x, \frac{1}{2}-y, \bar{z}$

where $x=0.126$, $y=0.218$, and $z=0.0625$.

The observed and calculated interplanar spacings and intensities are shown in Table I, where only those planes which predict observable intensities are listed. A projection on the xy plane of the distribution of oxygen ions corresponding to these conditions is shown in Fig. 2.

Each oxygen ion is surrounded by a somewhat distorted tetrahedron of oxygen ions very similar to the ice I arrangement.[3] The packing diameter of the oxygen ions has the same value 2.71A as was found for ice II. The axial ratios $1.73:1:1.22$ are also such as to permit the oxygen ions to lie in a unit cell on a hexagonal lattice of dimensions $a=5.87$A and $c=7.17$A. The proposed distribution, however, cannot be described by any hexagonal space group. The dotted lines in Fig. 2 indicate the xy projection of the hexagonal lattice.

The assignment of positions to the hydrogen atoms is necessarily arbitrary, since no x-ray evidence exists regarding this point. The distribution of oxygen atoms is such that it is not possible to assign two hydrogen atoms to each oxygen atom to form a water molecule with an H−O−H angle between 106°–109°, and at the same time obtain an electrostatically reasonable structure. Consequently, the procedure of Barnes[5] with ice I and the author[3] with ice II has been followed. It is assumed that each hydrogen ion lies on a line joining the center of an oxygen ion to the center of one of its nearest neighbors, and further that each hydrogen ion lies midway between the neighboring oxygen centers. This arrangement gives the necessary 32 ions of hydrogen per unit cell, is consistent with the accepted value

TABLE I.

hkl	*d*(calc.)	*d*(obs.)	*I*(calc.)	*I*(obs.)
002	3.58A	3.60A	227	v.s.
211	3.40A	3.39A	212	s.
020	2.94A	2.90A	203	s.
112	2.94A			
310	2.94A			
121	2.63A	2.66A	6.3	m.
400	2.55A	2.55A	127	s.
312	2.28A	2.28A	17.8	m.
022	2.27A			
321	2.12A	—	2.5	not obs.
402	2.08A	2.10A	52	s.
213	2.04A	2.07A	157	s.
130	1.93A	1.92A	97.5	s.
420	1.93A			
510	1.93A			
123	1.83A	1.86A	7.3	m.
231	1.77A	1.79A	9.5	m.
132	1.70A	1.68A	73.5	m-s
330	1.70A			
422	1.70A			
512	1.70A			
521	1.63A	1.62A	4.0	w.
323	1.63A			
611	1.59A	1.58A	7.5	m.
332	1.54A	1.53A	3.7	m-w
040	1.47A	1.48A	4.2	m.
233	1.46A	1.46A	19.9	m.
141	1.43A	1.43A	6.2	m.
530	1.42A			
710	1.42A			
523	1.38A	1.38A	1.5	w.
042	1.36A	1.36A	37.2	m-s
215	1.35A			
613	1.35A			
341	1.33A	1.32A	1.32	w.
532	1.32A			
712	1.32A			
125	1.29A	1.28A	10.4	m.
721	1.29A			
440	1.28A			
800	1.28A			
631	1.28A			
143	1.24A	1.23A	2.7	m.
325	1.20A	1.20A	7.0	m.
442	1.20A			
802	1.20A			
006	1.19A			

[5] W. H. Barnes, Proc. Roy. Soc. **A125**, 670 (1929).

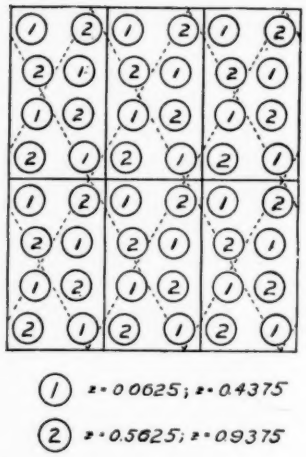

FIG. 2. Oxygen atoms, ice II.

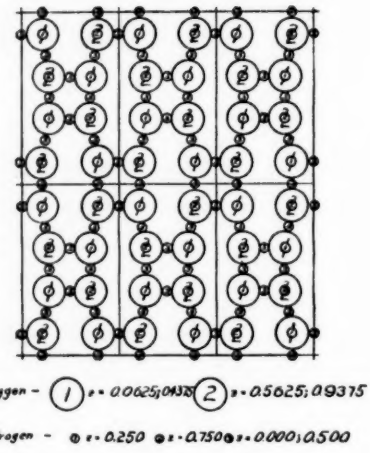

FIG. 3. Atomic distribution, ice III.

for the O−H−O packing distance, and satisfies all the symmetry requirements of space group V_h^{26}-Ibam. The coordinates obtained in this way for the hydrogen ions are as follows:

$\frac{1}{4}\,\frac{1}{4}\,0,\ \frac{1}{4}\,\frac{3}{4}\,0,\ \frac{3}{4}\,\frac{1}{4}\,0,\ \frac{3}{4}\,\frac{3}{4}\,0,\ \frac{3}{4}\,\frac{3}{4}\,\frac{1}{2},\ \frac{3}{4}\,\frac{1}{4}\,\frac{1}{2},\ \frac{1}{4}\,\frac{3}{4}\,\frac{1}{2},\ \frac{1}{4}\,\frac{1}{4}\,\frac{1}{2};$

$u00;\ u0\tfrac{1}{2};\ u+\tfrac{1}{2},\ \tfrac{1}{2},\ 0;\ u+\tfrac{1}{2},\ \tfrac{1}{2},\ \tfrac{1}{2};\ \bar{u}00;\ \bar{u}0\tfrac{1}{2};\ \tfrac{1}{2}-u,\ \tfrac{1}{2},\ 0;\ \tfrac{1}{2}-u,\ \tfrac{1}{2},\ \tfrac{1}{2};$ where $u=0.126$;

$0u0;\ 0u\tfrac{1}{2};\ \tfrac{1}{2},\ u+\tfrac{1}{2},\ 0;\ \tfrac{1}{2},\ u+\tfrac{1}{2},\ \tfrac{1}{2};\ 0\bar{u}0;\ 0\bar{u}\tfrac{1}{2};\ \tfrac{1}{2},\ \tfrac{1}{2}-u,\ 0;\ \tfrac{1}{2},\ \tfrac{1}{2}-u,\ \tfrac{1}{2};$ where $u=0.218$;

$0\tfrac{1}{2}u;\ \tfrac{1}{2}0u;\ \tfrac{1}{2},\ 0,\ u+\tfrac{1}{2};\ 0,\ \tfrac{1}{2},\ u+\tfrac{1}{2};\ 0\tfrac{1}{2}\bar{u};\ \tfrac{1}{2}0\bar{u};\ \tfrac{1}{2},\ 0,\ \tfrac{1}{2}-u;\ 0,\ \tfrac{1}{2},\ \tfrac{1}{2}-u;$ where $u=0.250$.

A projection of this arrangement on the xy plane is shown in Fig. 3.

The angles between the OH directions connected with any one oxygen ion are listed below.

91° 10′	108° 50′
83° 45′	108° 50′
140° 10′	108° 50′

Three of these angles—108° 50′—agree very closely with the 109° value used by Bernal and Fowler[6] in building up their solution for ice I. However, due to the fact that the ice III structure shown in Fig. 3 does not have trigonal symmetry about the z axis it is impossible to build up a complete structure associating two hydrogen ions with each oxygen ion, and keeping the angle between the OH directions constant at 108° 50′. This requires that the proposed ice III lattice be considered either as

1. A molecular lattice in which some of the bond angles are considerably strained.
2. An ionic lattice in which most of the OH bond angles satisfy the requirements of a molecular lattice.

The latter alternative was adopted in assigning positions to the hydrogen ions. The extreme slowness of the liquid—ice III reaction, and the great distance which the liquid can be subcooled with respect to ice III seem consistent with this viewpoint. Thus freezing under high pressure is assumed to be capable of changing the OH bond angles of the water molecule. However, it is also conceivable that high pressures squeeze the water molecules to such an extent that some of them might be broken up, which action would be reflected in the ice III structure. Unfortunately, this question cannot be settled on the basis of existing data since no measurements on the electrical conductivity of water at high pressures have been made.

The number and distance of various oxygen neighbors is shown in Table II. This compares with four neighbors at 2.74A and thirteen at 4.47A for ice I. As in the ice II structure[5] the increased density of ice III is seen to be the result of a relatively small change in the nearest neighbor distances of ice I—i.e., actual ionic compression—and a considerable decrease in the ice I next nearest neighbor distances—i.e., geometrical compression.

It is tempting to associate a distribution similar to ice III with Bernal and Fowler's water II.[6]

[6] Bernal and Fowler, J. Chem. Phys. **1**, 515 (1933).

TABLE II.

Number Oxygen Ions	Distance	Number Oxygen Ions	Distance
4	2.71A	1	4.98A
1	3.42A	2	5.11A
1	3.62A	1	5.75A
2	3.88A	2	5.78A
1	4.18A	2	5.87A
6	4.41A	2	5.92A
1	4.47A	4	5.94A
1	4.51A	1	6.10A
2	4.72A	1	6.13A
2	4.88A	4	6.45A

There is a rough qualitative agreement between their "quartz-like adjusted" distribution function, and the distribution function obtained from the ice III distribution. However, quantitative calculations regarding this point have not as yet been made, and further speculations regarding this point should await such a calculation.

The Ice I–Ice III Reaction

The volume loss or density increase of the ice forms with increasing pressure can be ascribed to two factors:

1. The actual loss of ionic volume—i.e., ionic compression.
2. The breaking down of the open spaces between ions as a result of ionic rearrangement—i.e., geometric compression.

As suggested by Bernal and Fowler[6] it seems reasonable to assume that the volume change of any one ice at different pressures inside its range of stability is due to the compression of the ions themselves—an assumption strictly true only for crystal structures without variable parameters. On this basis the O−H−O packing distance of ice I at the phase line dividing the ice I and ice III regions would be 2.71A. The O−H−O packing distance as determined by x-rays for ice III at −155°C and atmospheric pressure is 2.71A. In view of the stability of ice III outside the press and the results obtained from ice II[3] the O−H−O packing distance for ice III at the I–III phase line should differ at most only slightly from 2.71A. It would thus appear that the volume change accompanying the ice I–ice III reaction is due almost entirely to a geometrical rearrangement of the ions. Some idea as to the manner in which this rearrangement takes place can be obtained by noticing that the lengths along the z axis of the ice I and ice III unit cells are almost identical, when allowances are made for the effects of pressure and temperature. Both ice I and ice III are built up in a sort of pyramid structure.[3] It would thus seem reasonable to expect the ionic rearrangement to consist of a displacement of pairs of oxygen ions, having the same x and y coordinates, parallel to the xy plane. This can be illustrated by a reference to Fig. 2, Fig. 4 and Fig. 5. Fig. 4 shows the oxygen ions of ice I projected on the xy plane of an orthorhombic lattice. Fig. 5 shows the same oxygen ion pairs displaced parallel to the x axis. The continuous lines in Fig. 5 represent the x and y axes of the same orthorhombic lattice as Fig. 4. The dotted lines in Fig. 5 represent the x and y axes of an orthorhombic unit cell which contains sixteen oxygen ions distributed in accordance with the symmetry requirements of space group V_h^{26}-Ibam. The same unit cell having the proper experimental axial ratios is shown in Fig. 2. The volume decrease accompanying the ice I–ice III reaction is thus seen to be almost entirely a geometrical compression resulting from an oxygen ion rearrangement.

The compressibility of ice III is given by

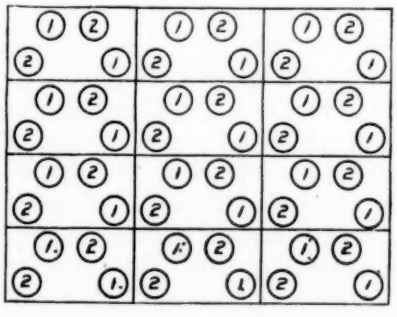

FIG. 4. Transition me chanism, ice I–ice III.

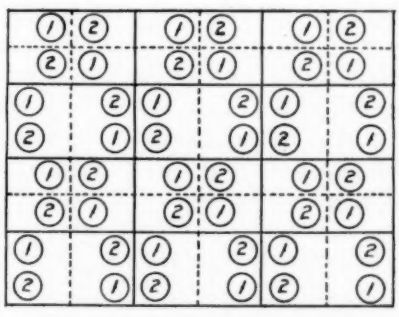

FIG. 5. Transition mechanism, ice I–ice III.

Bridgman[2] as 9.1×10^{-6} at 2000 atmospheres pressure, while that of ice I at the same pressure is given as 8×10^{-6}. The compressibility is thus seen to increase on changing over from ice I to ice III at the same pressure. This would seem to indicate either that the O−H−O packing distance increased slightly as a result of the change, or that the coordinates of the oxygen ions of ice III were not as independent of pressure as were those of ice I. The former possibility appears the more probable, although the point cannot be definitely settled since the temperature variation as a function of pressure of the oxygen ion volume is not definitely known.

The mechanism of this solid-solid reaction is also of interest in connection with several phenomena pointed out by Bridgman.[2] It is possible to carry ice I far into the ice III region by increasing the pressure at constant temperature, in fact so far as to meet the projection of the I–L curve—see Fig. 1—at which point the ice I melts. The probability of the reaction taking place increases with the temperature, and when the reaction takes place it does so very rapidly. These phenomena appear consistent with the transition mechanism just described. The initial displacements of the oxygen pairs parallel to the x axis require the breaking of electrostatic bonds, and also the transition of ions through regions partly occupied by other ions. The greater amplitude of thermal vibration at the higher temperatures increases the probability of such a reaction.

The latent heat change in the ice I–ice III reaction is small, and is either positive or negative depending on the temperature at which the reaction occurs. If, as was suggested in the case of ice II,[3] this latent heat is interpreted as resulting from the breaking of the OH bonds of the water molecule one would expect the latent heat of the ice I–ice III reaction to be smaller than that of the ice I–ice II reaction. The number of H−O−H bond angles having large deviations from the 103°–109° values of the water molecule is much greater in the case of ice II than ice III, and the latent heat of the ice I–ice II transition is much greater.

The Ice II–Ice III Reaction

The mechanisms of the ice I–ice III and the ice I–ice II reactions are very different. It has been shown before[3] that the breaking down of the ice I structure to form ice II consists of a slipping of oxygen ion layers relative to each other. The amount of slip under pressure is limited by the repulsive forces of the next nearest oxygen ion neighbors. The ice II–ice III transition depends on temperature only, and takes place immediately if the temperature is increased beyond a definite critical value.[2] This would seem to indicate a tendency of the H−O−H bonds to assume their molecular values as much as possible, once the temperature has been raised sufficiently to permit the oxygen ions to slip past each other, as pointed out in connection with the ice I–ice III transition. However, if pure ice III is cooled below the phase line the ice III–ice II reaction will probably not take place. The ice I-like structure of ice III is not easily broken by reducing the temperature, and runs most readily[2] when ice II nuclei are present in the apparatus. But even the presence of ice II nuclei is not sufficient to make the reaction go to completion at the lower temperatures as films showing both ice II and ice III in the same crystal mass have been obtained. In agreement with this is the observation of Bridgman that the ice I–ice II reaction runs slowly, and never seems to run to completion at the low temperatures −80°C.

As one would expect the latent heat involved in the ice II–ice III reaction is large, even greater than that of the ice I–ice II transition. The breaking up of the ice I-like bonds of ice III together with the fundamental rearrangement of the lattice is consistent with this picture. The change of volume is small compared to the volume changes in the ice I–ice II and the ice I–ice III reactions.

Liquid-Ice III Transition

It is not possible to describe with any degree of exactness the nature of the liquid-solid transition involving ice III. The latent heat given out on the freezing of ice III is approximately the same as that given out when ice I is formed, and the change in internal energy is about the same. The work done in forming both ices is of the same order of magnitude but the volume changes are in opposite directions, ice III decreasing five percent in volume on freezing. Bernal and Fowler[6] consider the ice I–liquid transition as equivalent

to molecular disorder plus a change of coordination, a change which involves large latent heat, a large volume change—usually negative—and the possibility of extensive overcooling as the liquid does not correspond in inner structure to the solid that crystallizes from it. The ice III–liquid transition differs from these conditions only in the volume change, which is both small and positive. There is no experimental evidence as to the nature of the water in contact with ice III other than the compressibility measurements of Bridgman. The great distance which the liquid can be subcooled with respect to ice III, and the slowness of the reaction would both seem to indicate that its internal structure differs somewhat from that of ice III. It does not seem probable, however, that the observed ice III structure would crystallize out of a quartz-like liquid.[6] It is more probable that the liquid in contact with ice III has a structure analogous to ice III. Numerous attempts have been made to fit the observed ice II and ice III data to a quartz-like structure, but the strong 002 reflection present in all possible interplanar spacing matches ruled out such a structure. The possibility of extending ice III-like water to water at atmospheric pressure requires a quantitative examination which has not as yet been made.

Other High Pressure Ice Results

Photographs have also been made of the ices formed in the regions V and VI—see Fig. 1. The diffraction patterns of ices formed in the V region indicated two different kinds of structures, although neither of these structures has been analyzed. The recent observations of Professor Bridgman that two different forms exist in this region, and to which he has assigned the numbers IV and V are thus confirmed. Both a powder pattern and a single crystal rotation pattern have been obtained of ice VI. However, the patterns of IV, V, and VI all indicated structures of too low symmetry to be analyzed with the present data. This would seem to indicate that the symmetry of a polymorphous ice form decreases as the pressure corresponding to its region of stability increases. Consequently, it appears very unlikely that any of the polymorphous ice forms are quartz-like in structure.[6]

Conclusions

1. On the basis of the structures so far analyzed the pressure corresponding to a region of stability and the coordination of the structure that is stable in that region seem to be independent; ice I, ice II, and ice III all having coordination numbers of four.

2. The O−H−O packing distance of the ices decreases with increasing pressure, and also with decreasing temperature. Both of these factors must be of the same order of magnitude since the polymorphous ice forms are stable at atmospheric pressure if the temperature is kept sufficiently low.

3. The volume decrease which accompanies the transitions to the high pressure ice forms is due almost entirely to the rearrangement of the ions in the crystal. Ionic compression takes place continuously with increasing pressure.

4. The mechanism of the solid-solid reactions can be interpreted in terms of simple ionic displacements.

5. It is possible to correlate the order of magnitude of the latent heat changes accompanying the solid-solid reactions with the relative number of large departures per unit cell from the normal H−O−H bond angles.

6. The x-ray evidence obtained from all the ice forms points to a lowering of symmetry with increasing pressure corresponding to the region of stability.

7. The lowering of symmetry with lowering of temperature of the region of stability—observed in many crystal forms—is in agreement with the observed symmetries of ice II and ice III.

The Vibration-Rotation Energy Levels of Polyatomic Molecules

I. Mathematical Theory of Semirigid Asymmetrical Top Molecules

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The exact classical kinetic energy for a system of point masses is obtained. From this the correct form for the quantum-mechanical Hamiltonian operator is derived. If the assumption of small vibrations is applied to this operator, the familiar approximation of a rigid top plus normal coordinate vibrator is obtained. In order to secure better approximations, in which larger amplitudes of vibration are admitted, a perturbation method is introduced which permits the change of moment of inertia with vibration, the coupling of rotation and vibration, and the centrifugal stretching effects to be taken into account. If the stretching terms alone are neglected, it is possible to reduce the secular equation for the rotational energy levels to the Wang form, except that "effective moments of inertia" must be used whose magnitude depends on the vibrational quantum state. The relation of these quantities to the equilibrium moments of inertia or to the instantaneous moments of inertia averaged over the vibrational motion is not simple, although the numerical deviation from them may not be great. In addition, for molecules with less than orthorhombic symmetry there is the further possibility that the orientation of the principal axes of inertia will vary with the vibrational quantum number. It is also pointed out that the Wang equation should not fit the data when a nearby vibrational state perturbs the state under examination or when the centrifugal effects are large. A method is indicated whereby the latter terms may in principle be calculated.

THE usual method of treating the rotational energy levels of polyatomic molecules has been to regard the molecule as a rigid top.[1] Recently, however, it has been realized that the rotational fine-structure is influenced by the nonrigidity of the molecule, especially through the coupling of the angular momenta of vibration and rotation.[2] Furthermore, it is well known that different empirical moments of inertia are required[3] in applying the Wang[1] secular equation for the asymmetric top to each vibration-rotation band, presumably due to the changing of the effective moments of inertia by the vibrational motion. Finally, the rigid top model does not allow centrifugal stretching effects, whereas such effects occur experimentally.

It is the purpose of this paper to give a rigorous treatment of the rotational energy levels of a system of point masses, representing the atoms, connected by forces such that the resulting system is semirigid; i.e., each mass vibrates about an equilibrium position which is fixed relative to the equilibrium positions of the other masses. In this treatment all the effects discussed above will enter and may be taken into account in principle to any desired degree of approximation.

CLASSICAL KINETIC ENERGY

In order to obtain the correct Schrödinger equation for the system of point masses, we shall first have to derive the classical kinetic energy. This we shall do using the angular velocity of a rotating system of axes fixed in the molecule and internal coordinates relative to these axes. The problem is conveniently set up vectorially. Let the position of the ith particle be given by the vector $\mathbf{r}_i$ from a point O, which is the origin of a moving (translating and rotating) system of coordinates. Let x_i, y_i, z_i be the components of $\mathbf{r}_i$ in the moving system of axes. The point O is in turn described by a vector $\mathbf{R}$ from a space-fixed origin. The equilibrium position of the ith particle is given by $\mathbf{a}_i$, which is a vector fixed to the rotating-axis system. We define the displacement vector $\boldsymbol{\varrho}_i$ by the equation $\boldsymbol{\varrho}_i = \mathbf{r}_i - \mathbf{a}_i$.

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[1] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931). H. B. G. Casimir. *The Rotation of a Rigid Body in Quantum Mechanics.* Dissertation (Leyden, 1931). The original treatments of the asymmetric top are, S. C. Wang, Phys. Rev. **34**, 243 (1929); H. A. Kramers and G. P. Ittmann, Zeits. f. Physik **53**, 553 (1929), etc.; O. Klein, Zeits. f. Physik **58**, 730 (1929).

[2] E. Teller and L. Tisza, Zeits. f. Physik **73**, 791 (1932); E. Teller, *Hand- und Jahrbuch d. chem. Physik*, Vol. 9 (1934), p. 125; J. H. Van Vleck, Phys. Rev. **47**, 487 (1935); C. Eckart, Phys. Rev. **47**, 552 (1935); H. A. Jahn, Ann. d. Physik **23**, 529 (1935); M. Johnston and D. M. Dennison, Phys. Rev. **48**, 868 (1935).

[3] R. Mecke. Zeits. f. Physik **81**, 313 (1933), etc.

If the rotating system of axes has an angular velocity ω and if the vector $\mathbf{v}_i$ is defined as the vector with components $\dot{x}_i$, $\dot{y}_i$, $\dot{z}_i$ in the moving system, then the velocity of the ith particle in space is[4]

$$\dot{\mathbf{R}}+\omega\times\mathbf{r}_i+\mathbf{v}_i. \tag{1}$$

Consequently the kinetic energy T of the whole system is given by

$$2T=\dot{R}^2\sum m_i+\sum m_i(\omega\times\mathbf{r}_i)\cdot(\omega\times\mathbf{r}_i)+\sum m_i v_i^2+2\dot{\mathbf{R}}\cdot\sum m_i\mathbf{v}_i+2\dot{\mathbf{R}}\times\omega\cdot\sum m_i\mathbf{r}_i+2\omega\cdot\sum m_i\mathbf{r}_i\times\mathbf{v}_i. \tag{2}$$

We have not yet defined the rotating system. Following Eckart,[5] we do so by introducing the conditions

$$\sum m_i\mathbf{v}_i=0 \quad \text{and} \quad \sum m_i\mathbf{a}_i\times\mathbf{v}_i=0. \tag{3}$$

The first of these implies also that $\sum m_i\mathbf{r}_i=0$, or that the origin of the moving system is at the center of gravity of the molecule. The second condition states that there is no angular momentum, to the first approximation (i.e., $\mathbf{a}_i$ replacing $\mathbf{r}_i$), relative to the moving system.

Replacing $\mathbf{r}_i$ by $\mathbf{a}_i+\varrho_i$ in the last term of Eq. (2) and using the conditions (3), we obtain

$$2T=\dot{R}^2\sum m_i+\sum m_i(\omega\times\mathbf{r}_i)\cdot(\omega\times\mathbf{r}_i)+\sum m_i v_i^2+2\omega\cdot\sum m_i\varrho_i\times\mathbf{v}_i. \tag{4}$$

The first term is the translational energy of the system and will be omitted hereafter because it can always be separated from the other terms. The second term is the rotational energy, the third the vibrational energy, and the last the coupling between rotation and vibration. By standard methods,[4] the kinetic energy expression above can be reduced to the form

$$2T=A\omega_x^2+B\omega_y^2+C\omega_z^2-2D\omega_x\omega_y-2E\omega_y\omega_z-2F\omega_z\omega_x+\sum m_i v_i^2+2\omega_x\sum m_i(\varrho_i\times\mathbf{v}_i)_x+2\omega_y\sum m_i(\varrho_i\times\mathbf{v}_i)_y+2\omega_z\sum m_i(\varrho_i\times\mathbf{v}_i)_z, \tag{5}$$

in which A, B, C are the instantaneous moments of inertia with respect to the moving x, y, z axes, respectively; D, E, and F are the products of inertia with respect to the x and y, y and z, z and x axes, respectively; ω_x, ω_y, ω_z are the components of the angular velocity ω of the rotating system of axes. It is to be emphasized that A, B, C, etc., are not constants, but are functions of the positions of the particles which change as the molecule vibrates.

[4] For a closely similar treatment of rigid bodies which gives more of the intermediate steps see L. Page, *Introduction to Theoretical Physics*, Chapter II.

[5] C. Eckart, Phys. Rev. **47**, 552 (1935).

Introduction of normal coordinates

It is now convenient to introduce a set of $3N-6$ internal coordinates, which are best chosen to be the normal coordinates Q_k of the vibration problem. These are defined in terms of the components $\xi_i/(m_i)^{\frac{1}{2}}$, $\eta_i/(m_i)^{\frac{1}{2}}$, and $\zeta_i/(m_i)^{\frac{1}{2}}$ of the displacement vector ϱ_i by the equations

$$\xi_i=\sum_k l_{ik}Q_k, \quad \eta_i=\sum_k m_{ik}Q_k, \quad \zeta_i=\sum_k n_{ik}Q_k, \tag{6}$$

in which ξ_i, η_i, ζ_i measure the displacement from the equilibrium position in terms of a mass-adjusted scale, and l_{ik}, m_{ik}, n_{ik} are constant coefficients.

Consequently, since the normal coordinates are normalized and orthogonal,

$$\sum m_i v_i^2=\sum(\dot{\xi}_i^2+\dot{\eta}_i^2+\dot{\zeta}_i^2)=\sum_k\dot{Q}_k^2, \tag{7}$$

and

$$\begin{aligned}\sum m_i(\varrho_i\times\mathbf{v}_i)_x&=\sum(\eta_i\dot{\zeta}_i-\zeta_i\dot{\eta}_i)=\sum_k\mathfrak{X}_k\dot{Q}_k,\\ \sum m_i(\varrho_i\times\mathbf{v}_i)_y&=\sum\mathfrak{Y}_k\dot{Q}_k,\\ \sum m_i(\varrho_i\times\mathbf{v}_i)_z&=\sum\mathfrak{Z}_k\dot{Q}_k,\end{aligned} \tag{8}$$

in which

$$\begin{aligned}\mathfrak{X}_k&=\sum_{i,l}(n_{ik}m_{il}-m_{ik}n_{il})Q_l,\\ \mathfrak{Y}_k&=\sum_{i,l}(l_{ik}n_{il}-n_{ik}l_{il})Q_l,\\ \mathfrak{Z}_k&=\sum_{i,l}(m_{ik}l_{il}-l_{ik}m_{il})Q_l.\end{aligned} \tag{9}$$

The kinetic energy is therefore

$$2T=A\omega_x^2+B\omega_y^2+C\omega_z^2-2D\omega_x\omega_y-2E\omega_y\omega_z-2F\omega_z\omega_x+2\omega_x\sum_k\mathfrak{X}_k\dot{Q}_k+2\omega_y\sum_k\mathfrak{Y}_k\dot{Q}_k+2\omega_z\sum_k\mathfrak{Z}_k\dot{Q}_k+\sum_k\dot{Q}_k^2. \tag{10}$$

Hamiltonian form

It is now necessary to express the kinetic energy in terms of the angular momenta instead of the angular velocities. The components of the total angular momentum are given by[6]

$$\begin{aligned} P_x &= \partial T/\partial\omega_x = A\omega_x - D\omega_y - F\omega_z + \sum \mathfrak{X}_k \dot{Q}_k, \\ P_y &= \partial T/\partial\omega_y = -D\omega_x + B\omega_y - E\omega_z + \sum \mathfrak{Y}_k \dot{Q}_k, \\ P_z &= \partial T/\partial\omega_z = -F\omega_x - E\omega_y + C\omega_z + \sum \mathfrak{Z}_k \dot{Q}_k. \end{aligned} \tag{11}$$

The momentum p_k, conjugate to Q_k, is

$$p_k = \partial T/\partial\dot{Q}_k = \dot{Q}_k + \mathfrak{X}_k\omega_x + \mathfrak{Y}_k\omega_y + \mathfrak{Z}_k\omega_z. \tag{12}$$

These equations may be solved for ω_x, ω_y, ω_z and the $\dot{Q}_k$'s in terms of P_x, P_y, P_z and the p_k's and the results when substituted in Eq. (10) lead to the Hamiltonian form of the kinetic energy. It is thus found (see fine print below) that the complete Hamiltonian form may be written

$$\begin{aligned} 2T = {} & \mu_{xx}(P_x - p_x)^2 + \mu_{yy}(P_y - p_y)^2 \\ & + \mu_{zz}(P_z - p_z)^2 + 2\mu_{xy}(P_x - p_x)(P_y - p_y) \\ & + 2\mu_{yz}(P_y - p_y)(P_z - p_z) \\ & + 2\mu_{zx}(P_z - p_z)(P_x - p_x) + \sum p_k^2. \end{aligned} \tag{13}$$

Here p_x, p_y, p_z are the components of angular momentum arising from vibration alone and are given by the expressions

$$p_x = \sum \mathfrak{X}_k p_k, \quad p_y = \sum \mathfrak{Y}_k p_k, \quad p_z = \sum \mathfrak{Z}_k p_k, \tag{14}$$

with $\mathfrak{X}_k$, $\mathfrak{Y}_k$, $\mathfrak{Z}_k$ defined by Eq. (9) above. The coefficients $\mu_{\alpha\beta}$ are functions only of the normal coordinates.

The following method was used to obtain the coefficients $\mu_{\alpha\beta}$ in Eq. (13). From Eqs. (10), (11) and (12) we have

$$2T = P_x\omega_x + P_y\omega_y + P_z\omega_z + \sum p_k\dot{Q}_k. \tag{15}$$

If we substitute in Eq. (15) the expression for $\dot{Q}_k$ obtained from the solution of Eq. (12), the kinetic energy becomes

$$2T = (P_x - p_x)\omega_x + (P_y - p_y)\omega_y + (P_z - p_z)\omega_z + \sum p_k^2. \tag{16}$$

Substituting in Eq. (11) the same expression for $\dot{Q}_k$ and rearranging, we have

$$\begin{aligned} P_x - p_x &= A'\omega_x - D'\omega_y - F'\omega_z, \\ P_y - p_y &= -D'\omega_x + B'\omega_y - E'\omega_z, \\ P_z - p_z &= -F'\omega_x - E'\omega_y + C'\omega_z, \end{aligned} \tag{17}$$

in which

$$\begin{aligned} & A' = A - \Sigma\mathfrak{X}_k^2; \quad B' = B - \Sigma\mathfrak{Y}_k^2; \quad C' = C - \Sigma\mathfrak{Z}_k^2; \\ & D' = D + \Sigma\mathfrak{X}_k\mathfrak{Y}_k; \quad E' = E + \Sigma\mathfrak{Y}_k\mathfrak{Z}_k; \quad F' = F + \Sigma\mathfrak{Z}_k\mathfrak{X}_k. \end{aligned} \tag{18}$$

If the inverse of transformation (17) is written

$$\begin{aligned} \omega_x &= \mu_{xx}(P_x - p_x) + \mu_{xy}(P_y - p_y) + \mu_{xz}(P_z - p_z), \\ \omega_y &= \mu_{yx}(P_x - p_x) + \mu_{yy}(P_y - p_y) + \mu_{yz}(P_z - p_z), \\ \omega_z &= \mu_{zx}(P_x - p_x) + \mu_{zy}(P_y - p_y) + \mu_{zz}(P_z - p_z), \end{aligned} \tag{19}$$

and if these expressions are substituted in Eq. (16), we obtain the form (13) of the kinetic energy.

Quantum-Mechanical Hamiltonian

In this section we shall obtain the Schrödinger wave equation (in operator form) corresponding to the classical Hamiltonian given above. The difficulty is that the Hamiltonian is expressed in terms of momenta which are not conjugate to any coordinates so that the customary procedure for transforming the Hamiltonian from the classical to the quantum-mechanical form requires a slight extension. It is well known that when the classical kinetic energy is given by

$$2T = \sum_{i,j} g_{ij}\dot{q}_i\dot{q}_j \tag{20}$$

in terms of the generalized coordinates q_i, and consequently by

$$2T = \sum_{i,j} g^{ij}p_ip_j \tag{21}$$

in terms of the momenta p_i conjugate to the q_i (g^{ij} are the elements of the matrix inverse to the matrix (g_{ij})), then the wave-mechanical Hamiltonian operator is[7]

$$\mathbf{H} = \tfrac{1}{2}g^{\frac{1}{4}}\sum_{i,j} \mathbf{p}_i g^{ij} g^{-\frac{1}{4}} \mathbf{p}_j + V. \tag{22}$$

Here $\mathbf{p}_i = (h/2\pi i)\partial/\partial q_i$, g is the determinant of the coefficients g^{ij}, and V is the potential energy.

If we now transform to a new set of momenta P_m which are not conjugate to any set of coordinates but which are defined by the transformation

$$p_i = \sum_m s_{im}P_m, \tag{23}$$

[6] The angular momentum is defined by $\mathbf{P} = \sum m_i\mathbf{r}_i \times \dot{\mathbf{r}}_i = \sum m_i[\mathbf{r}_i \times (\boldsymbol{\omega} \times \mathbf{r}_i)] + \sum m_i\mathbf{r}_i \times \mathbf{v}_i$. From this it can be seen that Eq. (11) is correct.

[7] See, for example, B. Podolsky, Phys. Rev. **32**, 812 (1928).

then $$2T=\sum_{m,\,n} G^{mn}P_mP_n, \tag{24}$$

with $$G^{mn}=\sum_{i,\,j} s_{im}g^{ij}s_{jn}. \tag{25}$$

We inquire concerning the condition under which it is possible to express the wave-mechanical Hamiltonian in a form analogous to Eq. (22), namely, as

$$\mathbf{H}=\tfrac{1}{2}G^{\frac{1}{4}}\sum_{m,\,n}\mathbf{P}_mG^{mn}G^{-\frac{1}{4}}\mathbf{P}_n+V, \tag{26}$$

in which G is the determinant of the matrix (G^{mn}). To obtain this condition we substitute in Eq. (26) the expression

$$\mathbf{P}_m=\sum_i s^{mi}\mathbf{p}_i, \tag{27}$$

which is the inverse of the transformation in Eq. (23). Noting that $G=s^2g$, where s is the determinant of the matrix (s_{im}), and using Eq. (25), we find

$$\mathbf{H}=\tfrac{1}{2}g^{\frac{1}{4}}\sum_{ijkm} ss^{mi}\mathbf{p}_is_{km}s^{-1}g^{kj}g^{-\frac{1}{4}}\mathbf{p}_j. \tag{28}$$

In order that Eq. (28) reduce to Eq. (22) the following condition must obviously be fulfilled:

$$\sum_{im} s^{mi}\mathbf{p}_is_{km}=(1/s)\mathbf{p}_ks. \tag{29}$$

If the kinetic energy of our system were expressed in terms of the Eulerian angles φ, θ, χ and the normal coordinates Q_k, together with the conjugate momenta p_φ, p_θ, p_χ and p_k, the Hamiltonian operator would assume the form (22). We wish to apply condition (29) to the transformation from the momenta p_φ, p_θ, p_χ, p_k to the set of momenta defined by Eqs. (11) and (12). The coefficients s^{mi} of Eq. (27) are readily obtained. For example, we can write for the x component of the total angular momentum

$$P_x=\frac{\partial T}{\partial\omega_x}=\frac{\partial T}{\partial\dot\varphi}\frac{\partial\dot\varphi}{\partial\omega_x}+\frac{\partial T}{\partial\dot\theta}\frac{\partial\dot\theta}{\partial\omega_x}+\frac{\partial T}{\partial\dot\chi}\frac{\partial\dot\chi}{\partial\omega_x}$$

$$=\frac{\partial\dot\varphi}{\partial\omega_x}p_\varphi+\frac{\partial\dot\theta}{\partial\omega_x}p_\theta+\frac{\partial\dot\chi}{\partial\omega_x}p_\chi$$

and similar expressions for P_y and P_z. The complete transformation corresponding to Eq. (27) is thus found to be*

$$\begin{aligned}P_x&=\sin\chi\,p_\theta-\cos\chi\csc\theta\,p_\varphi+\cos\chi\cot\theta\,p_\chi,\\ P_y&=\cos\chi\,p_\theta+\sin\chi\csc\theta\,p_\varphi-\sin\chi\cot\theta\,p_\chi,\\ P_z&=p_\chi,\quad p_k=p_k.\end{aligned} \tag{30}$$

The further transformation to the components of momenta defined by Eq. (17) and (14) is obviously

$$\begin{aligned}(P_x-p_x)&=P_x-\sum\mathfrak{X}_kp_k,\\ (P_y-p_y)&=P_y-\sum\mathfrak{Y}_kp_k,\\ (P_z-p_z)&=P_z-\sum\mathfrak{Z}_kp_k,\\ p_k&=p_k.\end{aligned} \tag{31}$$

It is easily verified that the condition (29) is satisfied by both of these transformations. Consequently we may write the Hamiltonian operator corresponding to the classical kinetic energy (13) as[8]

$$\mathbf{H}=\tfrac{1}{2}\mu^{\frac{1}{4}}\sum_{\alpha,\,\beta}(\mathbf{P}_\alpha-\mathbf{p}_\alpha)\mu_{\alpha\beta}\mu^{-\frac{1}{4}}(\mathbf{P}_\beta-\mathbf{p}_\beta)$$
$$+\tfrac{1}{2}\mu^{\frac{1}{4}}\sum_k\mathbf{p}_k\mu^{-\frac{1}{4}}\mathbf{p}_k+V, \tag{32}$$

in which α, β denote x, y or z and μ is the determinant of $(\mu_{\alpha\beta})$. When we expand this expression, noting that $\mathbf{P}_\alpha$ commutes with $\mathbf{p}_k$ and that the coefficients $\mu_{\alpha\beta}$ are functions only of the normal coordinates, we finally obtain as the desired form of the quantum-mechanical Hamiltonian operator

$$\mathbf{H}=\tfrac{1}{2}\sum_{\alpha,\,\beta}\mu_{\alpha\beta}\mathbf{P}_\alpha\mathbf{P}_\beta-\sum_\alpha h_\alpha\mathbf{P}_\alpha+\tfrac{1}{2}\sum_{\alpha,\,\beta}\mu^{\frac{1}{4}}\mathbf{p}_\alpha\mu_{\alpha\beta}\mu^{-\frac{1}{4}}\mathbf{p}_\beta$$
$$+\tfrac{1}{2}\sum_k\mu^{\frac{1}{4}}\mathbf{p}_k\mu^{-\frac{1}{4}}\mathbf{p}_k+V. \tag{33}$$

Here

$$h_\alpha=\tfrac{1}{2}\sum_\beta\{2\mu_{\alpha\beta}\mathbf{p}_\beta+(\mathbf{p}_\beta\mu_{\alpha\beta})+\mu_{\alpha\beta}\mu^{\frac{1}{4}}(\mathbf{p}_\beta\mu^{-\frac{1}{4}})\}, \tag{34}$$

in which $\mathbf{p}_\beta$ operates only on what is included in the parentheses.

* These equations may be determined from the vectorial relations between the components of $\boldsymbol{\omega}$ and $\dot\varphi$, $\dot\theta$, $\dot\chi$.

[8] When the dependence of $\mu_{\alpha\beta}$ on the normal coordinates is neglected this expression reduces to

$$\mathbf{H}=\tfrac{1}{2}\Sigma_\alpha(\mathbf{P}_\alpha-\mathbf{p}_\alpha)^2/I_\alpha+\tfrac{1}{2}\Sigma\mathbf{p}_k^2+V,$$

where I_α is a principal moment of inertia. This expression has also been justified by Van Vleck by another method, reference 2.

The Rigid Rotator Approximation

If the potential energy V has a deep and sharp minimum at the equilibrium configuration, the classical motion of the atoms will be limited to small regions near their equilibrium positions (for small values of the vibrational energy) and, quantum-mechanically, the vibrational wave functions will be appreciable only near this configuration. As a first approximation, we may therefore neglect all powers of Q_k but the zeroth power in the kinetic energy (retaining $V(Q_1\cdots)$, however), obtaining as the expression for the Hamiltonian operator

$$\tfrac{1}{2}(\mathbf{P}_x^2/A_0+\mathbf{P}_y^2/B_0+\mathbf{P}_z^2/C_0)+\tfrac{1}{2}\sum \mathbf{p}_k^2+V, \quad (35)$$

since $\mu_{xx}\rightarrow 1/A_0$, etc., when terms in Q_k are dropped. A_0, B_0, and C_0 are the equilibrium moments of inertia.

It is seen that the problem of finding the approximate energy levels is separable into two problems: the determination of the rotational energy levels from

$$\mathbf{H}_R{}^0=\tfrac{1}{2}(\mathbf{P}_x^2/A_0+\mathbf{P}_y^2/B_0+\mathbf{P}_z^2/C_0) \quad (36)$$

and the determination of the vibrational energies from the other terms. The vibrational problem is usually solved by the use of normal coordinates, while the rotational problem is that of the rigid asymmetrical top (if $A_0\neq B_0\neq C_0$) which has been solved[1] by Wang with Schrödinger mechanics and by Klein directly with operator calculus. By replacing p_θ by $(h/2\pi i)\partial/\partial\theta$, etc., in Eq. (30), the explicit expressions for the operators $\mathbf{P}_x$, $\mathbf{P}_y$ and $\mathbf{P}_z$ may be obtained. From these we can verify the commutation rules[9]

$$\begin{aligned}\mathbf{P}_x\mathbf{P}_y-\mathbf{P}_y\mathbf{P}_x&=(h/2\pi i)\mathbf{P}_z;\\ \mathbf{P}_y\mathbf{P}_z-\mathbf{P}_z\mathbf{P}_y&=(h/2\pi i)\mathbf{P}_x;\\ \mathbf{P}_z\mathbf{P}_x-\mathbf{P}_x\mathbf{P}_z&=(h/2\pi i)\mathbf{P}_y.\end{aligned} \quad (37)$$

Klein[1] used these relations and the fact that the operator for the total angular momentum, $\mathbf{P}_x^2+\mathbf{P}_y^2+\mathbf{P}_z^2$, has the eigenvalues $J(J+1)h^2/4\pi^2$ to obtain Wang's secular equation for the rotational energy levels. These levels are given by

$$W_{J,\sigma}=(h^2/8\pi^2)\{J(J+1)\tfrac{1}{2}(1/A_0+1/B_0)+[1/C_0-\tfrac{1}{2}(1/A_0+1/B_0)]\epsilon\}, \quad (38)$$

in which ϵ is a root of the secular equation of degree $2J+1$ in ϵ whose elements are

$$(K\,|\,K)=K^2-\epsilon, \quad (K\pm 2\,|\,K)=bf(J,K\pm 1), \text{ others zero}, \quad (39)$$

with $K=-J,\ -J+1,\ \cdots,\ +J$ and

$$b=\tfrac{1}{2}(1/A_0-1/B_0)\times[1/C_0-\tfrac{1}{2}(1/A_0+1/B_0)]^{-1}, \quad (40)$$

$$f(J,K)=-\tfrac{1}{2}\{[J^2-K^2][(J+1)^2-K^2]\}^{\frac{1}{2}}.$$

Higher Approximations for Asymmetrical Top Molecules

Perturbation theory

In order to get better approximations, in which finite amplitudes of vibration are considered, the full expression (33) for $\mathbf{H}$ must be used. We may, however, divide this into two parts, $\mathbf{H}^0$ and $\lambda\mathbf{H}'$, and apply perturbation theory. The unperturbed part $\mathbf{H}^0$ is given by

$$\mathbf{H}^0=\mathbf{H}_R{}^0+\mathfrak{V} \quad (41)$$

in which $\mathbf{H}_R{}^0$ has been given in Eq. (36) while $\mathfrak{V}$ is the vibration operator, comprising the last three terms of Eq. (33). The perturbation $\lambda\mathbf{H}'$ consists of those terms of $\mathbf{H}$ not included in $\mathbf{H}^0$ and is to be considered as of smaller magnitude than $\mathbf{H}^0$. Let us set up the matrices for $\mathbf{H}^0$ and $\lambda\mathbf{H}'$ in terms of basis functions $\psi_R\psi_V$, where ψ_R is a function of the rotational coordinates only and has quantum numbers denoted by R, while ψ_V is a function of the internal coordinates (normal coordinates) only and has the quantum number V. Furthermore, let the ψ_V be normalized and orthogonal solutions of the vibrational wave equation. Then $\mathbf{H}^0$ will be diagonal in V but not necessarily diagonal in R, because ψ_R is not necessarily a solution of the rotational problem. $\lambda\mathbf{H}'$ will not be diagonal in either R or V but its elements will be small.

Under these circumstances, it has been shown, for example by Jordahl,[10] that it is possible to

[9] It is to be noted that the sign is different in these relations, which refer to moving axes, from that for fixed axes. See Klein and Casimir, reference 1. The expressions for the operators $\mathbf{P}_x$, $\mathbf{P}_y$, $\mathbf{P}_z$ in Eq. (30) are the same whether the molecule is rigid or not, even though in the latter case the total angular momentum includes vibrational momentum.

[10] O. M. Jordahl, Phys. Rev. **45**, 87 (1934).

find a transformation which transforms the matrix $\mathbf{H}=\mathbf{H}^0+\lambda\mathbf{H}'$ into a matrix in which the only terms nondiagonal in V are of order λ^2 or higher. These nondiagonal terms may be neglected in obtaining the energy correct to λ^2. With their neglect the transformed matrix factors into smaller matrices $\mathfrak{H}$, one for each vibrational state, whose elements $\mathfrak{H}_{R,\,R'}$ are labeled by the R quantum numbers only, it being understood that these elements are diagonal in V. $\mathfrak{H}$ is given by

$$\mathfrak{H}=\mathfrak{H}_0+\lambda\mathfrak{H}_1+\lambda^2\mathfrak{H}_2+\cdots, \tag{42}$$

in which the elements of $\mathfrak{H}_0+\lambda\mathfrak{H}_1$ are given by $H^0_{RV,\,R'V}+\lambda H'_{RV,\,R'V}$ or $H_{RV,\,R'V}$, while the elements of $\lambda^2\mathfrak{H}_2$ are

$$\lambda^2(\mathfrak{H}_2)_{R,\,R'}=\sum_{R'',\,V''}{}'\frac{H_{RV,\,R''V''}H_{R''V'',\,R'V}}{h\nu_{V,\,V''}}, \tag{43}$$

in which it has been assumed that the spacing of the rotational levels is small compared with that of the vibrational levels so that $W^0_{RV}-W^0_{R''V''}$ can be replaced by $W^0_V-W^0_{V''}=h\nu_{VV''}$, the difference of the vibrational energies. Terms in which $V''=V$ are omitted in the summation.

Fig. 1 shows the nature of the matrix $\mathbf{H}$ before and after transformation ($\mathbf{H}$ is really an infinite matrix). Before transformation $\mathbf{H}$ can be factored and therefore separated into a problem of rotation and one of vibration only by neglecting terms of order λ (as was done in the rigid rotator approximation). After transformation the factoring is possible when terms nondiagonal in V of order λ^2 are neglected. However, this approximation, in addition to giving the energy levels correct in terms of the order λ^2, also differs from the first approximation in that the small rotational matrices $\mathfrak{H}$ are not the same for each vibrational state because the elements of $\lambda\mathfrak{H}_1$ and $\lambda^2\mathfrak{H}_2$ are functions of V.

Nature of the rotational energy matrix $\mathfrak{H}$

By the use of the transformation just discussed, the infinite energy matrix has been factored into smaller *rotational* matrices (shaded squares in Fig. 1b). The eigenvalues of one of these small matrices are the rotational energy levels for that particular vibrational state and are accurate in terms of order λ^2. Let us now consider the general nature of one of these small matrices.

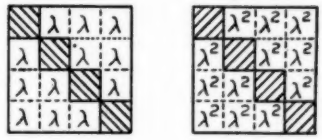

FIG. 1. The energy matrix $\mathbf{H}$ before and after transformation. The blocks have different sets of vibrational quantum numbers VV'; each block should be subdivided into elements with different rotational sets RR'. The shaded areas are of zeroth order in λ; the unshaded areas of first or second order as indicated.

The elements of zeroth and first order in λ are given by

$$(\mathfrak{H}_0)_{R,\,R'}+\lambda(\mathfrak{H}_1)_{R,\,R'}=H_{RV,\,R'V}$$
$$=\int\psi_V^*\psi_R^*\mathbf{H}\psi_V\psi_{R'}d\tau,$$

where $\mathbf{H}$ is the complete Hamiltonian given in Eq. (33). Each of the terms of $\mathbf{H}$, except the purely vibrational terms, is a product of a rotational factor and a vibrational factor. A typical example is $\mu_{xy}\mathbf{P}_x\mathbf{P}_y$. Inserting in the integral, we get

$$\int\psi_V^*\psi_R^*\mu_{xy}\mathbf{P}_x\mathbf{P}_y\psi_V\psi_{R'}d\tau$$
$$=\int\psi_V^*\mu_{xy}\psi_Vd\tau_V\int\psi_R^*\mathbf{P}_x\mathbf{P}_y\psi_{R'}d\tau_R \tag{44}$$
$$=\overline{\mu_{xy}}(P_xP_y)_{R,\,R'},$$

where the bar denotes the quantum-mechanical average. $\overline{\mu_{xy}}$ is independent of the quantum number R. Therefore if we denote by $\mathbf{P}_x\mathbf{P}_y$ not only the operator but also the matrix with elements $(P_xP_y)_{R,\,R'}$, then we can write a matrix equation

$$\mathfrak{H}_0+\lambda\mathfrak{H}_1=\mathbf{W}_V+\tfrac{1}{2}\sum_{\alpha,\,\beta}\overline{\mu_{\alpha\beta}}\mathbf{P}_\alpha\mathbf{P}_\beta-\sum_\alpha\overline{h_\alpha}\mathbf{P}_\alpha, \tag{45}$$

in which $\mathbf{W}_V$ is a diagonal matrix in R whose diagonal elements are all equal to W_V^0, the vibrational energy. This term comes from the purely vibrational terms of $\mathbf{H}$.

The terms of order λ^2 can now be considered. They are given by Eq. (43). The element $(\mathfrak{H}_2)_{R,\,R'}$ is a sum of terms because $H_{RV,\,R''V''}$ is a sum. A typical term is

$$-\tfrac{1}{2}\sum_{R'',\,V''}{}'(\mu_{zz}P_z^2)_{RV,\,R''V''}$$
$$\times(h_yP_y)_{R''V'',\,R'V}/h\nu_{V,\,V''}, \tag{46}$$

We have just seen, however, that elements such

as $(\mu_{xx}P_x^2)_{RV,\,R''V''}$ factor, becoming $(\mu_{xx})_{V,\,V''}\cdot(P_x^2)_{R,\,R''}$. Therefore we get

$$-\tfrac{1}{2}\sum_{R''}(P_x^2)_{RR''}(P_y)_{R'',\,R'}\times\sum_{V''}{}'(\mu_{xx})_{V,\,V''}(h_y)_{V'',\,V}/h\nu_{V,\,V''} \quad (47)$$

$$=-\tfrac{1}{2}(P_x^2P_y)_{R,\,R'}\sum_{V''}{}'(\mu_{xx})_{V,\,V''}(h_y)_{V'',\,V}/h\nu_{V,\,V''}.$$

Here again each term reduces to a constant independent of R times a matrix element of a monomial in $\mathbf{P}_x$, $\mathbf{P}_y$, $\mathbf{P}_z$.

It is thus evident that the matrix $\mathfrak{H}$ can be written as a polynomial in the matrices $\mathbf{P}_x$, $\mathbf{P}_y$, $\mathbf{P}_z$ with constant coefficients which are formed from integrals involving the vibrational wave functions. Further examination shows that the linear terms in $\mathbf{P}_x$, $\mathbf{P}_y$, $\mathbf{P}_z$ vanish identically and the cubic terms vanish or reduce to quadratic terms. The coefficients of $\mathbf{P}_x$, $\mathbf{P}_y$, and $\mathbf{P}_z$ in $\mathfrak{H}$ are $-\bar{h}_x$, $-\bar{h}_y$, and $-\bar{h}_z$, respectively. $\mathfrak{H}$ and $\mathbf{P}_\alpha$ are Hermitian matrices; consequently the matrix formed from the elements $(h_\alpha)_{V,\,V'}$ is Hermitian. But h_α is a pure imaginary operator, since every term contains $(h/2\pi i)$ and all the other quantities are real. Furthermore, for asymmetric top molecules (excluding cases of accidental degeneracy) ψ_V is real. Consequently,[11] the diagonal term

$$(h_\alpha)^*_{V,\,V}=-(h_\alpha)_{V,\,V}=(h_\alpha)_{V,\,V}=0.$$

The cubic terms in $\mathbf{P}_x$, $\mathbf{P}_y$, $\mathbf{P}_z$ can likewise be eliminated. The coefficients of $\mathbf{P}_x^3$, $\mathbf{P}_y^3$, and $\mathbf{P}_z^3$ vanish; for example

$$\tfrac{1}{2}\mathbf{P}_x^3\sum_{V''}{}'\{(\mu_{xx})_{V,\,V''}(h_x)_{V'',\,V}+(h_x)_{V,\,V''}(\mu_{xx})_{V''V}\}/h\nu_{V,\,V''}=0$$

because $(h_x)_{V,\,V''}=-(h_x)_{V'',\,V}$ and $(\mu_{xx})_{V,\,V''}=(\mu_{xx})_{V'',\,V}$, since h_x is a pure imaginary operator while μ_{xx} is a real one. The other cubic terms all occur in pairs of the type $\mathbf{P}_x^2\mathbf{P}_y-\mathbf{P}_y\mathbf{P}_x^2$ with some coefficient. But

$$\mathbf{P}_x^2\mathbf{P}_y-\mathbf{P}_y\mathbf{P}_x^2=\mathbf{P}_x(\mathbf{P}_x\mathbf{P}_y-\mathbf{P}_y\mathbf{P}_x)+(\mathbf{P}_x\mathbf{P}_y-\mathbf{P}_y\mathbf{P}_x)\mathbf{P}_x=(h/2\pi i)(\mathbf{P}_x\mathbf{P}_z+\mathbf{P}_z\mathbf{P}_x) \quad (48)$$

from the commutation relations, Eq. (37), so that these reduce to quadratic terms.

[11] This can also be proved by partial integration.

The conclusion is that, as a consequence of the perturbation treatment, we may write the small rotational matrix $\mathfrak{H}=\mathfrak{H}_0+\lambda\mathfrak{H}_1+\lambda^2\mathfrak{H}_2$, which corresponds to a single vibrational quantum state, as a polynomial of the following sort in the matrices $\mathbf{P}_x$, $\mathbf{P}_y$, and $\mathbf{P}_z$:

$$\mathfrak{H}=\mathbf{W}_V+\tfrac{1}{2}\sum_{\alpha,\,\beta}\sigma_{\alpha\beta}\mathbf{P}_\alpha\mathbf{P}_\beta+\tfrac{1}{4}\sum_{\alpha,\,\beta,\,\gamma,\,\delta}\tau_{\alpha\beta\gamma\delta}\mathbf{P}_\alpha\mathbf{P}_\beta\mathbf{P}_\gamma\mathbf{P}_\delta, \quad (49)$$

in which the coefficients $\sigma_{\alpha\beta}$ and $\tau_{\alpha\beta\gamma\delta}$ depend upon the vibrational quantum state to which $\mathfrak{H}$ corresponds. If the vibrational wave functions are known with sufficient accuracy, the coefficients can be computed. The matrices for $\mathbf{P}_x$, $\mathbf{P}_y$ and $\mathbf{P}_z$ are known,[12] so that in principle the secular equation for the rotational problem can be set up, including quartic terms in $\mathbf{P}_x$, $\mathbf{P}_y$ and $\mathbf{P}_z$. The solution of this problem would permit the change of moment of inertia with vibration, the coupling of rotation and vibration, and the centrifugal stretching effects to be taken into account.

Unfortunately, the error introduced by using the harmonic oscillator approximation to ψ_V may be as large as the perturbation effects we have been considering (the anharmonicity will be important in μ_{xx}, for example) so that one cannot, at the present time, evaluate the coefficients theoretically. However, we can by making certain approximations reduce the secular equation to the Wang form [Eq. (39)], in which A_0, B_0, and C_0 are replaced by three empirical parameters to be determined from experimental data. This is the procedure which has generally been used, without justification; we shall show that it is often, but not always, justified.

Transformation to Wang form

In order to obtain the Wang form of the secular equation, the quartic terms in $\mathbf{P}_x$, $\mathbf{P}_y$, $\mathbf{P}_z$ in Eq. (49) must be neglected. These terms, by analogy with diatomic molecules, correspond at least in part to centrifugal stretching effects. Experimentally it is observed that such effects are detectable for higher rotational states; they are not therefore entirely negligible. For low

[12] O. Klein, Zeits. f. Physik **58**, 730 (1929).

rotational states, however, they are small. A rough method of classification of terms in $\mathfrak{H}$ according to magnitude is by powers of the vibrational frequency ν. On this basis the coefficients of the quadratic terms are of order ν^0, plus corrections of order ν^{-1} and ν^{-1}, etc., while the coefficients of the quartic terms are of order ν^{-2}. For this reason we omit the quartic terms for the present.

In case no other vibrational state perturbs the state under investigation, we can therefore, with the omission of the quartic terms, write the Hamiltonian $\mathfrak{H}$ in the form

$$\mathfrak{H}=\mathbf{W}_V+\tfrac{1}{2}\{\sigma_{xx}\mathbf{P}_x^2+\sigma_{yy}\mathbf{P}_y^2+\sigma_{zz}\mathbf{P}_z^2 +\sigma_{xy}(\mathbf{P}_x\mathbf{P}_y+\mathbf{P}_y\mathbf{P}_x)+\sigma_{yz}(\mathbf{P}_y\mathbf{P}_z+\mathbf{P}_z\mathbf{P}_y) +\sigma_{zx}(\mathbf{P}_z\mathbf{P}_x+\mathbf{P}_x\mathbf{P}_z)\}. \quad (50)$$

This quadratic form may be reduced to principal axes by means of an orthogonal transformation on the matrices (or operators) $\mathbf{P}_x$, $\mathbf{P}_y$, $\mathbf{P}_z$, the transformation coefficients being ordinary numbers.[13] For molecules with orthorhombic symmetry, it can be shown from symmetry arguments that the cross terms in Eq. (50) vanish, so that no transformation is required. For molecules of lower symmetry, since the coefficients $\sigma_{\alpha\beta}$ depend upon the vibrational quantum state, the transformation, and consequently the orientation of the principal axes of inertia, will also vary somewhat with the vibrational state.

When the reduction to principal axes has been made, there results

$$\mathfrak{H}'=\mathbf{W}_V+\tfrac{1}{2}\{\mathfrak{P}_x^2/A_e+\mathfrak{P}_y^2/B_e+\mathfrak{P}_z^2/C_e\} \quad (51)$$

with

$$\mathfrak{P}_x^2+\mathfrak{P}_y^2+\mathfrak{P}_z^2=\mathbf{P}_x^2+\mathbf{P}_y^2+\mathbf{P}_z^2. \quad (52)$$

Furthermore the commutation rules for $\mathfrak{P}_x$, $\mathfrak{P}_y$ and $\mathfrak{P}_z$ are the same as those given in Eq. (37) for $\mathbf{P}_x$, $\mathbf{P}_y$ and $\mathbf{P}_z$.[14] Consequently, the problem is now formally identical with the rigid asymmetric top previously discussed, except that A_0, B_0 and C_0 must be replaced by A_e, B_e and C_e. The energy levels are given by the Wang equation [Eqs. (39) and (40)] with these new "effective moments of inertia." For orthorhombic molecules, $\sigma_{\alpha\alpha}$ is given by

$$\sigma_{\alpha\alpha}=\tfrac{1}{2}\overline{\mu_{\alpha\alpha}}+\sum_{V'}{}'(h_\alpha)_{VV'}(h_\alpha)_{V'V}/h\nu_{VV'} -(h/2\pi i)\sum_{V'}{}'\{(\mu_{\alpha\beta})_{VV'}(h_\gamma)_{V'V} -(\mu_{\alpha\gamma})_{VV'}(h_\beta)_{V'V}\}/h\nu_{VV'}. \quad (53)$$

It is seen that even in this simplest case, in which $\sigma_{xx}=1/A_e$, etc., A_e, B_e and C_e are not simply related to either the equilibrium moments of inertia A_0, B_0 and C_0 or the instantaneous moments of inertia A, B, and C. Therefore, the geometrical interpretation which has been given these quantities for excited vibrational states of observed molecules, for example water, may be misleading, if A_e, B_e and C_e differ appreciably from A_0, B_0 and C_0.

Centrifugal expansion terms

For energy levels with high J values, the quartic terms in $\mathbf{P}_x$, $\mathbf{P}_y$ and $\mathbf{P}_z$ in Eq. (49) will be of importance, since they correspond to centrifugal expansion of the molecule. In the general case there are a great many of these terms. The coefficient of the term $\mathbf{P}_\alpha\mathbf{P}_\beta\mathbf{P}_\gamma\mathbf{P}_\delta$, where α, β, γ, δ are selected from x, y, and z, is

$$\tfrac{1}{4}\sum'(\mu_{\alpha\beta})_{V,\,V'}(\mu_{\gamma\delta})_{V',\,V}/h\nu_{V,\,V'}. \quad (54)$$

In specific examples, many of these coefficients may vanish. Since the matrices for $\mathbf{P}_x$, $\mathbf{P}_y$ and $\mathbf{P}_z$ have been given, the contributions of these quartic terms to the secular equation can be computed. It is planned to discuss these in a later paper.

Accidental degeneracy

In case another vibrational state V'' has an energy close to the state V under consideration, the treatment given in this paper may break down. If the matrix element $H'_{RV,\,R''V''}$ is not very small, the term $H_{RV,\,R''V''}H_{R''V'',\,R'V}/h\nu_{V,\,V''}$ in Eq. (43) will be very large for such an accidental degeneracy and the perturbation technique used will not hold. Such cases are quite likely to occur in practice. The modifications of

[13] We are indebted to Professor J. H. Van Vleck for suggesting this method of reduction, as well as for calling our attention to the possibility of using the perturbation technique described earlier.

[14] The properties of the components of angular momentum should be independent of the choice of rotating axes. A more explicit proof can easily be given, however.

the theory necessary for treating such cases will be given in a subsequent paper.

Conclusion

It has been shown that the rotational energy levels of a semirigid asymmetric polyatomic molecule are given by the Wang equation for the rigid rotator with three "effective moments of inertia" if no accidental degeneracy occurs, and if centrifugal stretching terms are small enough to neglect. If these conditions are not fulfilled, the Wang equation may not apply.

In conclusion, we should like to thank Professor J. H. Van Vleck for several important suggestions.

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The Relative Atomic Weight of Oxygen in Water and in Air

A Discussion of the Atmospheric Distribution of the Oxygen Isotopes and of the Chemical Standard of Atomic Weights

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A difference in the density of water made from atmospheric oxygen plus tank hydrogen and aqueous oxygen plus tank hydrogen is interpreted as indicating that the atomic weight of oxygen in the air is 0.000108 atomic weight units heavier than the oxygen of Lake Michigan water. This observation finds experimental confirmation in the work of several other investigators and can be applied in certain cases to the reinterpretation of already existing data, clarifying several anomalous and inexplicable effects. The difference in atomic weights can be accounted for quantitatively by assuming that an isotopic exchange equilibrium of the type discussed by Urey and Greiff occurs at a temperature of −50°C in the lower regions of the stratosphere. The distribution of oxygen isotopes in the atmosphere is calculated by means of the usual hypsometric equation, but the separation due to gravity is not sufficient to explain quantitatively the excess atomic weight of atmospheric oxygen. The chemical and physical standards of atomic weights are discussed and the proposal is made that a single standard based on the mass of a pure isotope such as protium be adopted.

THE original discovery of isotopes gave rise to a considerable number of researches designed to test the constancy of chemical atomic weights of elements from a variety of natural sources, but no variation in the weights was observed, leading Aston,[1] for example, to conclude "that the evolution of the elements must have been such as to lead to a proportionality of isotopes of the same element which was constant from the start, and, since we know of no natural process of separation, has remained constant ever since." However, shortly after the discovery of deuterium, slight differences in the density of water from many sources were observed;[2] these differences were smaller than the experimental errors involved in previous atomic weight determinations, which explains why they had not been noted hitherto, but to the present time, however, no one has determined whether these differences in density are caused by variations in the isotopic composition of hydrogen or oxygen, the differences being usually attributed to variations in the abundance of deuterium.

Since the atomic weight of oxygen is the basis for the chemical atomic weight scale, it is especially interesting and important to know whether the isotopic ratios of oxygen in different compounds are the same. Manian, Urey and Bleakney[3] in a careful research investigated the relative abundance of the oxygen isotopes in

[1] F. W. Aston, *Mass-Spectra and Isotopes* (Edward Arnold and Company, London, 1933), p. 188.

[2] For a review see H. C. Urey and G. K. Teal, Rev. Mod. Phys. **7**, 34 (1935).

[3] S. H. Manian, H. C. Urey and W. Bleakney, J. Am. Chem. Soc. **56**, 2601 (1934). This paper contains references to earlier work. See also W. Bleakney and J. A. Hipple Jr., Phys. Rev. **47**, 800 (1935).

stone meteorites and found no variations, but their mass-spectrograph method was not as sensitive as the density of water method and could not demonstrate differences of the order of a few p.p.m. Smythe[4] also using the mass-spectrograph method determined the ratio $[O^{16}]/[O^{18}]$ in oxygen evolved from lead dioxide. Since his ratio was somewhat lower than that calculated from band spectra data, he postulated that there might have been a separation of the isotopes of oxygen in the formation of the lead dioxide, but Taylor and Gould[5] found no difference in the ratio of $[O^{16}]/[O^{18}]$ between the first and last fraction of oxygen evolved from lead dioxide. Urey and Greiff[6] calculated theoretically that in many chemical reactions isotopic exchanges could occur at equilibrium which could give rise to a slight variation in the atomic weights of the elements involved, and they stated that their calculations showed that the accuracy with which chemical atomic weights could be determined was limited by these isotopic exchanges. Weber, Wahl and Urey[7] proved experimentally that the bringing of carbon dioxide into equilibrium with water resulted in a concentration of O^{18} in the carbon dioxide to just the extent calculated by Urey and Greiff. They did not investigate, however, any natural compounds to see if these isotopic exchanges took place in nature. Furthermore, the author has shown[8] that it is possible to carry out certain chemical reactions involving water and carbon dioxide without any measurable isotopic exchange taking place.

In the investigation of benzene for its deuterium content and of Nevada hot springs water for its deuterium content, data were obtained by the author which made possible a calculation of the relative atomic weight of oxygen in Lake Michigan water and in air. It was found that water made from atmospheric oxygen plus tank hydrogen was 4.6 p.p.m. heavier than water made from aqueous oxygen plus tank hydrogen. This conclusion has already been communicated[9] in a brief note, but the value of 4.6 p.p.m. given there is uncertain because of the following facts: First, Linde oxygen was used instead of atmospheric oxygen, which made necessary the introduction of a correction factor; second, the hydrogen used was not from the same tank in each case and although the two hydrogens were compared, it is felt that this introduces the possibility of another experimental error; third, the necessary electrolyses were carried out a month or so apart instead of consecutively, thereby possibly allowing a change in the electrode surface which would alter the fractionation factor; and finally the density measurements were made weeks apart with a possible although not likely change in the method in the interim. It was concluded that a much more reliable value for the difference in the atomic weights of oxygen from the two sources could be obtained by carrying out a research with the sole purpose in view of measuring this difference.

Experimental

Two series of experiments were carried out using a slightly different electrolytic technique in the two cases. In both series oxygen of the air was converted into water by burning air with excess tank hydrogen over a copper catalyst. Excess hydrogen was used in order to eliminate any possible separation of the oxygen isotopes. Since the hydrogen of this water was different in atomic weight from the hydrogen of normal water, it was necessary to separate the oxygen in these two waters from their hydrogen by electrolysis and to convert both oxygens again to water by using hydrogen from the same tank. In this way the density of water made from tank hydrogen plus oxygen originally from the air could be compared with the density of water made from the same tank hydrogen plus oxygen originally from Lake Michigan water in order to compare the atomic weight of oxygen from the two sources. Two electrolysis cells were constructed so that they could be operated until a residue of about 40 cc remained in each cell. The electrodes were made of nickel and the electrolyte was 4 percent sodium hydroxide.

[4] W. R. Smythe, Phys. Rev. **45**, 299 (1934).
[5] H. S. Taylor and A. J. Gould, J. Am. Chem. Soc. **56**, 1823 (1934).
[6] H. C. Urey and Lotti J. Greiff, J. Am. Chem. Soc. **57**, 321 (1935).
[7] L. A. Weber, M. H. Wahl and H. C. Urey, J. Chem. Phys. **3**, 129 (1935).
[8] M. Dole, J. Am. Chem. Soc. in press.
[9] M. Dole, J. Am. Chem. Soc. **57**, 2731 (1935).

The hydrogen from the electrolysis was rejected while the oxygen passed first over a hot copper oxide tube to remove traces of hydrogen, then through a soda-lime drying tower, and finally over hot copper where it was converted to water with tank hydrogen. The hydrogen was passed through roughly in an equivalent amount. A separation of the isotopes of oxygen or of hydrogen may have occurred at this point although experiments described elsewhere indicated that any such separation is negligible.[8] If the same separation occurred in all the experiments, no error in the final result would be admitted.

Methods of purifying the water and of measuring the density have already been described.[8]

Data for the electrolyses and densities are given in Table I. Volumes of water are expressed in cc, temperatures in degrees C, and densities in p.p.m. The first horizontal column under series I gives the total water added to the electrolysis cell in the normal water and air water experiments, the second horizontal column the number of cc of water collected in two fractions by combining the cell oxygen with tank hydrogen in the normal water and air water experiments, the third horizontal column the volume of cell residue in the two electrolyses, the fourth horizontal column the water lost in the electrolysis process. Density measurements were made on the first and second fraction of the water obtained in the electrolysis of the normal and air waters, respectively; these results are given in terms of temperature differences between the temperature of floating equilibrium of the totally immersed float for ordinary water and the water under investigation in the horizontal column entitled "temperature of floating equilibrium." The horizontal column labeled "temperature difference between corresponding air and normal water" gives first, the difference between the temperature of floating equilibrium of the first electrolytic fraction of air water and the first electrolytic fraction of normal water, and second, the corresponding difference between the second fraction of the two waters. It should be noted that although the densities of the first and second fractions of each water are different, as is to be expected, nevertheless the difference between the first fraction in each case and the difference between the second fraction in each case are equal. The data for series II have similar meanings although here two separate electrolyses were carried out instead of taking two fractions of water during one electrolysis in each case.

TABLE I. *Electrolysis and density data.*

	SERIES I			
	NORMAL WATER		AIR WATER	
	I	II	I	II
Water added to cell	1150		1200	
Water collected	405	347	450	470
Cell residue	120		150	
Water lost in process	278		130	
Temperature of floating equilibrium	(−0.054) −0.051	−0.047 −0.046	−0.026 −0.025	−0.020 −0.020
Temperature difference between corresponding air and normal water	(0.028) 0.026	0.027 0.026		
Av. Density difference	0.026 6.0			

	SERIES II			
	NORMAL WATER		AIR WATER	
	I	II	I	II
Water added to cell	600	610	600	590
Water collected	450	465	450	440
Cell residue	60	66	70	68
Water lost in process	90	79	80	82
Temperature of floating equilibrium	−0.049 −0.049	−0.050 −0.049	−0.024 −0.022	−0.025 −0.022
Temperature difference between corresponding air and normal water	0.025 0.027	0.025 0.027		
Av. Density difference	0.026 6.0	0.026		

In the first series all the normal water was electrolyzed and then all the air water. In the second series the two electrolyses of the normal water alternated with the two of air water. The results of the two series agree within the accuracy of the temperature measurements, the accepted difference in density between water made from oxygen of the air and water made from aqueous oxygen being 6.0 ± 0.6 p.p.m. The reliability of the data can be tested by calculating the fractionation factor for the oxygen isotopes, α_0. Before electrolysis the air water was 3.9 p.p.m. less dense than normal and after electrolysis it was 5.9 p.p.m., less dense than normal, the difference -2.0 p.p.m. being due to the electrolytic fractionation of the oxygen isotopes since the hydrogen was tank hydrogen in the two waters. A change in density of 2 p.p.m. in the water on electrolysis is equivalent to a value of α_0 equal to 1.009 in close agreement with

the value 1.008 given by Johnston[10] and the value 1.0088 given by Selwood, Taylor, Hipple and Bleakney.[11]

A difference of density of 6.0±0.6 p.p.m. due to oxygen in the water is equivalent to a difference in the atomic weight of oxygen in air and in water of 0.000108±0.00001 atomic weight units, the oxygen in the air being the heavier.[12]

Experimental Confirmation in work of Other Investigators, and Applications

The above conclusion that the atomic weight of oxygen from air is slightly greater than that from water is confirmed qualitatively by data already published by a number of other investigators. Hall and Johnston[13] burned oxygen from normal water with tank hydrogen and air with the same hydrogen. The latter water was denser than the former by about 4 p.p.m. in qualitative agreement with our finding of 6 p.p.m. However, they burned the oxygen in large excess of hydrogen and the hydrogen in a large excess of air, so that not too much reliance on their figure of 4 p.p.m. can be given. Greene and Voskuyl[14] burned tank hydrogen with air obtaining water heavier than normal. It is difficult to see why this water is heavier than normal unless it is caused by the oxygen of the air being denser than normal. Washburn, Smith and Smith[15] burned commercial electrolytic hydrogen which they state should be lighter than normal with air obtaining water of normal density. If the hydrogen is lighter than normal, then the oxygen of the air must be heavier than that of normal water.

Many investigators (including the author) have burned organic compounds with oxygen from the air, interpreting the excess density of the resulting water as demonstrating an excess concentration of deuterium in the organic compound. Such data will now have to be reinterpreted.*

Table II. *Recalculation of the data of Washburn, Smith and Smith.* Changes in density (in p.p.m.) on electrolysis.

Number of Liters Collected	Recombined Gases	Cell O with "Normal" H (W.S. and S.)	Cell H with "Normal" O (W.S. and S.)	Cell O with Normal H Corrected	Cell H with Normal O Corrected
1	−20.5	−13.2	−7.8	−7.2	−13.8
10	−17.1	−11.0	−6.2	−5.0	−12.2
20	−14.8	−10.5	−5.6	−4.5	−11.6
30	−14.1	−8.0	−5.5	−2.0	−11.5
50	−10.8	−6.3	−3.6	−0.3	−9.6
75	−7.3	−5.0	−2.0	+1.0	−8.0
105	−5.0	−3.0	− .1	+3.0	−6.1
124	−3.1	−2.0	+ .1	+4.0	−5.9
150	−1.5	−1.1	+ .2	+4.9	−5.8

Washburn, Smith and Smith[16] have presented some interesting data concerning the electrolytic separation of the isotopes of both oxygen and hydrogen. They first tested the atomic weight of their commercial (electrolytic) hydrogen by burning it with air obtaining water of normal density. They concluded that their hydrogen was normal, but as stated above, their hydrogen must have been lighter than normal since the oxygen of the air is heavier than normal. (By "normal" is meant the same as in normal water.) A correction of about +6 p.p.m. (assuming that their water is the same in density as Lake Michigan water) should be applied to their data labeled "Cell O with normal H" and a correction of −6.0 p.p.m. should be applied to their data labeled "Cell H with normal O." Such corrections completely alter the nature of their results as can be seen from Table II where their original data are tabulated along with the new corrected data. The greater decrease in density of the different waters in the first stages of electrolysis is now seen to be due to the hydrogen fractionation instead of as formerly to the oxygen fractionation.[17] This is a much more

[10] H. L. Johnston, J. Am. Chem. Soc. **57**, 484 (1935).

[11] P. W. Selwood, H. S. Taylor, J. A. Hipple, Jr. and Walker Bleakney, J. Am. Chem. Soc. **57**, 642 (1935).

[12] Dr. E. R. Smith has kindly pointed out to us that the difference in the isotopic composition of the air oxygen and water oxygen might not be the same after electrolysis as before because of a greater absolute electrolytic separation in the case of the air oxygen. On calculation, however, this error was shown to be only 0.1 p.p.m. because of the low value of the fractionation factor for oxygen and therefore negligible.

[13] W. H. Hall and H. L. Johnston, J. Am. Chem. Soc. **57**, 1515 (1935).

[14] C. H. Greene and R. J. Voskuyl, J. Am. Chem. Soc. **56**, 1649 (1934).

[15] E. W. Washburn, E. R. Smith and F. A. Smith, Bur. Standards J. Research **13**, 599 (1934).

* This has been done by the author, J. Am. Chem. Soc., in press.

[16] E. W. Washburn, E. R. Smith and F. A. Smith, Bur. Standards J. Research **13**, 599 (1934); E. R. Smith and M. Wojciechowski, ibid. **15**, 187 (1935).

[17] The author, M. Dole, J. Am. Chem. Soc., **57**, 2731 (1935) incorrectly stated that Washburn, Smith and Smith concluded that the oxygen isotopes fractionate more rapidly than those of hydrogen on electrolysis. They had concluded that the initial change of density of the water on electrolysis was due more to the oxygen than to the hydrogen, not that $\alpha O > \alpha H$.

reasonable conclusion. However, a most surprising observation is made when one examines the density of the cell-O-with-normal-hydrogen-water in the later stages of electrolysis. *The atomic weight of the oxygen now coming off is greater than that of the water being added!* It is difficult to explain this if we assume the correctness of the experimental measurements. It appears as if the surface condition of the electrodes must have changed during the electrolysis so that instead of the electrolytic fractionation being favored in the electrode reaction, it is the equilibrium reaction of Urey and Greiff that is being favored.*

Selwood, Taylor, Hipple and Bleakney[18] have calculated the fractionation factor for the oxygen isotopes from Washburn, Smith and Smith's data to be 1.062 for the first stage of electrolysis. This figure is known to be too high, but a calculation based on the corrected data of Table II yields the factor 1.03 which is more reasonable although still not in complete agreement with the factor given by Selwood, Taylor, Hipple and Bleakney. A recalculation of the oxygen fractionation factor from the data of Greene and Voskuyl[19] gives α_0 equal to 1.013, a value close to that of Selwood and co-workers and to that of Johnston (1.01).[20]

Theoretical

There are numerous postulates that one can make explaining the observed difference between the atomic weights of oxygen in air and in water. Smythe[21] suggests that "most of the oxygen on the earth has been used in oxidizing the earth's crust and only a small fraction of one percent remains in the air. It is possible that some concentration, probably of the O^{16}, has taken place in this process so that the ratio $[O^{16}]/[O^{18}]$ for air is above average." A more reasonable explanation is that the O^{16} reacted more rapidly with the metals and with hydrogen than did O^{18} so that it is the O^{18} that is concentrated in the air. Unfortunately this hypothesis cannot be tested quantitatively not only because of the lack of adequate theory, but also because there is no reason to suppose that the atomic weight of atmospheric oxygen would remain constant since the time that the atmosphere was first formed. It is more plausible to believe that there are processes going on at the present time which can account for a natural difference in the isotopic ratios. These processes may be divided into two groups, first, those occurring on the earth's surface and those occurring in the upper regions of the earth's atmosphere.

Urey and Greiff[6] calculated from spectroscopic and vapor pressure data the O^{18} enrichment factor for the equilibrium

$$2H_2O^{18}(l)+O_2{}^{16}\rightleftarrows 2H_2O^{16}(l)+O_2{}^{18} \qquad (1)$$

to be 1.006 at 25°C and 1.010 at 0°C. If the assumption is made that oxygen can be brought into equilibrium with water,[22] by some process occurring on the earth's surface such as contact catalysis or the catalyzing action of plant or animal life bringing the oxygen into equilibrium with carbon dioxide and hence with water, then we should expect from equilibrium (1) that the oxygen of the air would be richer in O^{18} than the oxygen of ocean water to the extent of 1.3 p.p.m. in terms of water density at 25° and 2.2 p.p.m. at 0°C. Since we find 4.4 p.p.m.,[23] it is evident that any such equilibrium as (1) occurring at normal temperatures fails to account quantitatively for the observed effect.

Professor Urey[24] has suggested that perhaps the oxygen is brought into equilibrium with water through the action of solar ultraviolet radiation in the upper regions of the atmosphere. Assuming that such an effect is most pronounced in the stratosphere, or isothermal portion of the atmosphere, at a height of 20 kilometers where the ultraviolet radiation produces the greatest

* The positive values show that the oxygen coming off is heavier than the oxygen being added, not that it is heavier than the oxygen in the electrolyte.

[18] P. W. Selwood, H. S. Taylor, J. A. Hipple, Jr. and W. Bleakney, J. Am. Chem. Soc. **57**, 642 (1935).

[19] C. H. Greene and R. J. Voskuyl, J. Am. Chem. Soc. **56**, 1649 (1934).

[20] H. L. Johnston, J. Am. Chem. Soc. **57**, 484 (1935).

[21] W. R. Smythe, Phys. Rev. **45**, 299 (1934).

[22] There is, roughly, 10^3 times more oxygen in the water on the earth's surface than in the whole atmosphere, as can be calculated from the data given by Longwell, Knopf and Flint, *A Textbook of Geology* (John Wiley and Sons, Inc., N. Y., 1932) and by Humphreys, *Physics of the Air* (McGraw-Hill Book Co., New York, 1929), p. 76, hence we can assume that the isotopic ratio in water remains constant as the above equilibrium is set up.

[23] Correcting our value of 6.0 p.p.m. for the difference in density of ocean water and fresh water due to a difference in the isotopic composition of oxygen yields 4.4 p.p.m., *vide infra*.

[24] Private communication.

density of ozone,[25] it is possible to calculate the fractionation factor since the temperature for this part of the stratosphere is known to be −50°C or 223°A.[26] The fractionation fraction, α', for the equilibrium

$$2H_2O^{18}+O_2^{16}\rightleftarrows O_2^{18}+2H_2O^{16} \qquad (2)$$

is given by the equation

$$(\alpha')^2=K=f_{O_2^{18}}\cdot f^2_{H_2O^{16}}/f_{O_2^{16}}\cdot f^2_{H_2O^{18}}, \qquad (3)$$

where

$$f_{O_2^{18}}/f_{O_2^{16}}=1.3424 \exp (129.78/2T) \qquad (4)$$

and

$$f_{H_2O^{18}}/f_{H_2O^{16}}=1.1813 \exp (20.698/T) \qquad (5)$$

on inserting the numerical constants as given by Urey and Greiff, and omitting terms negligible at 273°A and below. Urey and Greiff state that their equation is valid at ordinary temperatures and above, but it should be also nearly valid at 223°A inasmuch as the water and oxygen molecules must still retain vibrational and rotational energies at this temperature. At 223°A α' is 1.034, but this value must be divided by 1.014 to obtain the fractionation factor for equilibrium (1); we are assuming, therefore, that the water which enters into equilibrium (2) in the stratosphere eventually diffuses to the earth's surface and gets into equilibrium with the water of the ocean. The calculated over-all fractionation factor for the equilibrium

$$2H_2O^{18}(\text{ocean})+O_2^{16}(\text{stratosphere}) \rightleftarrows 2H_2O^{16}(\text{ocean})+O_2^{18}(\text{stratosphere}) \qquad (6)$$

is, therefore, 1.020 or 4.4 p.p.m. in terms of water density. To this a correction of −0.2 p.p.m. should be applied to account for the fact that the equilibrium constant of the equilibrium

$$O_2^{16}+O_2^{18}\rightleftarrows 2O^{16}O^{18} \qquad (7)$$

is equal to 3.988 instead of 4.000 at 223°A;[27] the final value being 4.2 p.p.m. in terms of water density.

But in the experimental work presented above the atomic weight of oxygen of the air was compared with the atomic weight of oxygen in Lake Michigan water and not that of the ocean; a correction must be applied, therefore, to allow for the difference in the atomic weight of oxygen in Lake Michigan water and ocean water. Gilfillan[28] found on an average 2.3 p.p.m. excess density of Atlantic Ocean water over Cambridge, Mass. tap water, Greene and Voskuyl[29] found 1.8 p.p.m. and Wirth, Thompson and Utterback[30] found 1.47 p.p.m. for the average density difference between several samples of Pacific Ocean water and water of the Cedar River, State of Washington. Lake Michigan water has the same density as Cambridge, Mass., tap water,[31] but a comparison of Lake Michigan water with the State of Washington water has not yet been carried out to the author's knowledge. Assuming that they are identical, and averaging the three density differences given above, the figure 1.9 p.p.m. results for the density difference between purified ocean and fresh water. Of this difference we shall assume that 1.6 p.p.m.[28] is due to the difference in isotopic composition of the oxygen. We should add, therefore, approximately 1.6 p.p.m. to the value of 4.2 p.p.m., obtaining 5.8 p.p.m. as the calculated density difference between water composed of atmospheric oxygen and the oxygen of Lake Michigan water. This value agrees with the observed data given above within the experimental error, and indicates that the Urey and Greiff isotopic exchange equilibrium can account quantitatively for the effect providing the equilibrium is brought about at a sufficiently cold temperature. However, there may be isotopic exchanges occurring at warmer temperatures on the earth's surface which would tend to lower the value of 5.8 p.p.m. calculated for −50°C, so we should expect the observed value to be somewhat less than 5.8 p.p.m. This calculation indicates, therefore, that isotopic exchanges occur to a greater extent in the lower regions of the stratosphere than they do on the earth's surface.

In the isothermal portion of the atmosphere, the stratosphere, there are no winds or tempera-

[25] Private communication from Dr. O. R. Wulf. See also R. W. Ladenburg, J. Opt. Soc. Am. **25**, 259 (1935).
[26] R. W. Ladenburg, J. Opt. Soc. Am. **25**, 259 (1935).
[27] In calculating the equilibrium constant of (7) $\tilde{\omega}_{O^{16}O^{18}}$ was taken as 1540.6, $I_{O^{18}O^{16}}/I_{O_2^{16}}$ as 1.0598 and $I_{O_2^{18}}/I_{O^{16}O^{18}}$ as 1.0616.
[28] E. S. Gilfillan, Jr., J. Am. Chem. Soc. **56**, 406 (1934).
[29] C. H. Greene and R. J. Voskuyl, J. Am. Chem. Soc. **56**, 1649 (1934).
[30] H. E. Wirth with T. G. Thompson and C. L. Utterback, J. Am. Chem. Soc. **57**, 400 (1935).
[31] Private communication from Dr. C. H. Greene.

TABLE III. *Calculated partial pressures in millimeters of Hg, of the isotopes of molecular oxygen and water in the stratosphere.*

ALTITUDE (km)	$p_{O_2^{18}}$	$p_{O^{16}O^{18}}$	$p_{O^{18}O^{18}}$	$p_{H_2O^{16}}$	$p_{H_2O^{18}}$	α_{O_2}	α_{H_2O}
11	35.039	.14016	1.4×10^{-4}	1.677×10^{-2}	3.226×10^{-5}	1.000	1.000
20	7.3780	.02675	2.4×10^{-5}	6.981×10^{-3}	1.218×10^{-5}	1.103	1.102
30	1.3066	4.248×10^{-3}	3.5×10^{-6}	2.637×10^{-3}	4.130×10^{-6}	1.230	1.228
50	.040981	1.071×10^{-4}	7.0×10^{-8}	3.761×10^{-4}	4.745×10^{-7}	1.531	1.524
70	1.285×10^{-3}	2.701×10^{-6}	1.4×10^{-9}	5.365×10^{-5}	5.451×10^{-8}	1.903	1.892
90	4.031×10^{-5}	6.811×10^{-8}	2.9×10^{-11}	7.653×10^{-6}	6.263×10^{-9}	2.368	2.347
110	1.264×10^{-6}	1.717×10^{-9}	5.9×10^{-13}	1.092×10^{-6}	7.195×10^{-10}	2.944	2.918

ture gradients of any moment, so it is believed that the gases of the atmosphere distribute themselves in the earth's gravitational field in accordance with the well-known hypsometric equation which is

$$\log p=\log p_0-\frac{0.014837}{T}\cdot\frac{M}{Ma}(h-h_0), \qquad (8)$$

where Ma is the molecular weight of dry air, 28.97, M the molecular weight of the gas whose partial pressure is p at height h and p_0 at height h_0, the heights being expressed in units of meters, and T is the average absolute temperature of the stratosphere, −55°C according to Humphreys.[32] The partial pressures of several isotopic species have been calculated by means of Eq. (8) from the beginning of the stratosphere, (11 kilometers) to a height of 110 kilometers. The results are given in Table III where the last two columns show the extent to which the relative concentration of O^{18} atoms changes with height for both oxygen and water, α_{O_2} being the atom fraction of O^{18} in molecular oxygen at 11 kilometers divided by the same quantity at the other altitudes (the concentration of $O^{18}O^{18}$ being taken into consideration) and α_{H_2O} the atom fraction of O^{18} in the water vapor present at 11 kilometers divided by the same quantity at other altitudes. The atom fraction of O^{18} is not, of course, the same for molecular oxygen and water at 11 kilometers. The data of Table III indicate that at 20 kilometers where we have assumed the Urey and Greiff isotopic exchanges to come to equilibrium, the relative concentrations of O^{18} in oxygen and water are substantially the same as they are in the troposphere so that we do not need to correct our calculations based on Urey and Greiff's theory for any gravitational fractionation of the oxygen isotopes.

If the hypsometric Eq. (8) is valid, the data of Table III also indicate that there is a considerable variation in the concentration of O^{18} in the atmosphere with increasing altitude, and one is led to wonder if the relatively greater settling of molecules containing O^{18} in the atmosphere is responsible for the increased atomic weight of oxygen in the air as compared to that of oxygen in water. If the isotopic composition of oxygen was constant throughout the atmosphere and the earth when the atmosphere and the earth's crust were first formed, and later became altered in the atmosphere due to gravitational settling, we should expect just such a variation in the atomic weight of oxygen as we have reported above. Taking 0.002 as the atom fraction of O^{18} in the oxygen of the troposphere, and using other data and equations given by Humphreys[32] it is possible to calculate that in the entire atmosphere there are approximately 361.6×10^{17} moles of $O^{16}O^{16}$, 1.431×10^{17} moles of $O^{18}O^{16}$ and 0.0014×10^{17} moles of $O^{18}O^{18}$ which means that the atom fraction of O^{18} in oxygen for the entire atmosphere is 0.001979. The fractionation factor due to gravity is therefore 0.002000/0.001979 or 1.011 which is equivalent to 2.4 p.p.m. in terms of density of water. Adding 1.6 p.p.m. for the difference in density between the ocean water and fresh water due to the oxygen isotopic variation, we obtain 4.0 p.p.m. density difference instead of 6.0 p.p.m. as experimentally observed. It appears, therefore, that the explanation based on the Urey and Greiff isotopic exchange theory is more plausible that the gravitational theory as it predicts values in better quantitative agreement with actual fact although the gravitational theory could be improved by assuming a slight

[32] W. J. Humphreys, *Physics of the Air*, Chapter V (McGraw-Hill Book Company, Inc., New York, 1929). There does not seem to be at present enough quantitative information to include atomic oxygen in Table III although it apparently exists to a very great extent in the upper regions of the stratosphere, see O. R. Wulf, J. Opt. Soc. Am. **25**, 231 (1935).

difference in the atomic weight of oxygen between air and water when the atmosphere was first formed.

The hypsometric Eq. (8) gives partial pressures for the different molecular isotopes of oxygen which satisfy equilibrium (7) at every height.

The Standard of Chemical and Physical Atomic Weights

The "Fifth Report of the Committee on Atomic Weights of the International Union of Chemistry"[33] gives the atomic weight of oxygen as 16.0000. This is, of course, by definition, but we now have to ask ourselves, is this the atomic weight of oxygen in air or in water? If we take the atomic weight of oxygen in Lake Michigan water to be exactly 16.000000, then the atomic weight of oxygen in air is 16.000108. Measurements[34] of the density of water from Nevada hot springs indicate that if the atomic weight of oxygen in Nevada hot springs water is exactly 16.000000, then the atomic weight of oxygen in Lake Michigan water is 16.000034 and the atomic weight of oxygen in air is 16.000142. Clearly oxygen is not a suitable substance on which to base the standard of chemical atomic weights if we wish to express the atomic weight of oxygen or of other substances to six or more figures. The physicists have long since abandoned the element oxygen as the standard of reference in mass-spectrographic work, taking instead the isotope of oxygen of mass sixteen. This standard, however, is not a good one for chemists, inasmuch as there is no easy method suitable for the isolation of isotopically pure O^{16} isotope. It seems also to be losing favor with the physicists; for example, Bethe[35] states "The question of changing to the scale He=4.0000 might be reconsidered at this moment when all atomic weights have to be changed anyhow." Helium would be a bad choice from the chemist's point of view, on account of its chemical inertness.

Because of the possibility of isotopic separation and exchange in chemical reactions or physical processes, the logical substance on which to base the atomic weight scale should be a pure isotope, preferably the isotope of hydrogen of mass one or the element sodium which at the present time seems to be isotopically pure. Protium can be obtained easily in pure isotopic form in large quantities, it is chemically active and appears to be "elementary" matter when nuclear disintegration experiments are considered. The mass of protium, however, should be set at a value which would keep the element oxygen as near sixteen as possible so that there would be no need of changing our present atomic weights except in the fourth or fifth figure. Unfortunately at the present time there appears considerable uncertainty in the ratio of the O^{16} and H^1 masses so that[36] the time does not appear to be quite yet ripe for changing the standard of atomic weights from oxygen to another element. It is to be hoped, however, that the chemists will soon give up their chemical scale to adopt one based on a pure isotope and that the physicists will change their isotopic scale to bring it into accord with the chemical atomic weights, thereby rectifying the confusing situation of two atomic mass scales, an isotopic scale and a chemical element scale.

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Note added to proof: The January number of Bull. Chem. Soc. Japan, p. 36, Volume 11, contains a preliminary announcement by N. Morita and T. Titani of some work which is closely similar to our work described above which we first announced in the December number of J. Am. Chem. Soc. Morita and Titani's results, which are not given in detail, confirm ours within 2 p.p.m., but their experimental procedure is open to criticism since they did not put their air-oxygen water through the same process of electrolysis, etc., as their water-oxygen water.

[33] J. Am. Chem. Soc. **57**, 787 (1935).
[34] M. Dole, Science, in press.
[35] H. Bethe, Phys. Rev. **47**, 633 (1935).
[36] See, for example, H. Bethe, Phys. Rev. **47**, 633 (1935); and Oliphant, Kempton and Rutherford, Proc. Roy. Soc. **A150**, 252 (1935).

The Limiting High Temperature Rotational Partition Function of Nonrigid Molecules

I. General Theory. II. CH_4, C_2H_6, C_3H_8, $CH(CH_3)_3$, $C(CH_3)_4$ and $CH_3(CH_2)_2CH_3$. III. Benzene and Its Eleven Methyl Derivatives[1]

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I. The method given by Eidinoff and Aston for calculating the limiting high temperature rotational partition function has been further simplified. An important special case, comprising molecules which may be represented by a rigid framework to which symmetrical tops are attached in any position is developed. II. The methods of the preceding part are applied to the series of methyl derivatives of methane, and to the completely nonrigid molecule *n*-butane. The calculated entropies at 25°C show the same general variation with chain length and number of branches as has been found experimentally from the third law. III. The entropies of all the isomeric methyl derivatives of benzene are calculated. Comparison with third law values for the liquids is hampered by lack of reliable vapor pressure data and of vibration frequencies, but there are no major discrepancies which must be attributed to either the calculated or the observed entropies.

I. General Theory

In a recent article Eidinoff and Aston[3] have developed a powerful method for calculating the classical rotational partition function for nonrigid molecules. They prove that when the kinetic energy can be written as a positive-definite symmetric quadratic form

$$T=(1/2)\sum_{i=1}^{s}\sum_{j=1}^{s}R_{ij}\dot{q}_i\dot{q}_j \qquad (1)$$

and the potential energy is zero, then the classical partition function is

$$Q=(2\pi kT/h^2)^{s/2}\int\cdots\int[R]^{\frac{1}{2}}dq_1\cdots dq_s, \qquad (2)$$

where $[R]$ is the determinant formed by the R_{ij}. They did not carry the general theory beyond this point, although they worked out a number of special cases. It is possible, however, to develop a general procedure by which $[R]$ can be obtained without calculating all the terms in T.

Consider any convenient set of three orthogonal axes X, Y, Z fixed in the molecule, with origin at the center of gravity. For a nonrigid molecule, fixed axes mean merely axes which move in some specified unique way as the internal coordinates change. Let the coordinates of the ith atom referred to the X, Y, Z axes be x_i, y_i, z_i, each of which is in general a function of $s-3$ internal angular variables. Then the coordinates of the ith atom referred to U, V, W axes fixed in space and related to the X, Y, Z axes by Eulerian angles θ, φ, χ are

$$\begin{aligned} u_i&=a_{11}x_i+a_{12}y_i+a_{13}z_i,\\ v_i&=a_{21}x_i+a_{22}y_i+a_{23}z_i,\\ w_i&=a_{31}x_i+a_{32}y_i+a_{33}z_i, \end{aligned} \qquad (3)$$

where

$$\begin{aligned} a_{11}&=\sin\varphi\cos\chi+\cos\theta\cos\varphi\sin\chi,\\ a_{12}&=-\sin\varphi\sin\chi+\cos\theta\cos\varphi\cos\chi,\\ a_{13}&=\sin\theta\cos\varphi,\\ a_{21}&=-\cos\varphi\cos\chi+\cos\theta\sin\varphi\sin\chi,\\ a_{22}&=\cos\varphi\sin\chi+\cos\theta\sin\varphi\cos\chi,\\ a_{23}&=\sin\theta\sin\varphi,\\ a_{31}&=-\sin\theta\sin\chi,\\ a_{32}&=-\sin\theta\cos\chi,\\ a_{33}&=\cos\theta. \end{aligned} \qquad (4)$$

It is then readily shown that

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[3] Eidinoff and Aston, J. Chem. Phys. **3**, 379 (1935).

$$\begin{aligned}\dot{u}^2+\dot{v}^2+\dot{w}^2=&\dot{x}^2+\dot{y}^2+\dot{z}^2+2(\dot{x}y-\dot{y}x)(-\dot{\varphi}\cos\theta\\&-\dot{\chi})+2(\dot{x}z-\dot{z}x)(\dot{\theta}\sin\chi-\dot{\varphi}\sin\theta\cos\chi)\\&+2(\dot{y}z-\dot{z}y)(\dot{\theta}\cos\chi+\dot{\varphi}\sin\theta\sin\chi)\\&+x^2[\dot{\theta}^2\sin^2\chi-2\dot{\theta}\dot{\varphi}\sin\theta\sin\chi\cos\chi\\&+\dot{\varphi}^2(1-\sin^2\theta\sin^2\chi)+2\dot{\varphi}\dot{\chi}\cos\theta+\dot{\chi}^2]\\&+y^2[\dot{\theta}^2\cos^2\chi+2\dot{\theta}\dot{\varphi}\sin\theta\sin\chi\cos\chi\\&+\dot{\varphi}^2(1-\sin^2\theta\cos^2\chi)+2\dot{\varphi}\dot{\chi}\cos\theta+\dot{\chi}^2]\\&+z^2[\dot{\theta}^2+\dot{\varphi}^2\sin^2\theta]+2xy[\dot{\theta}^2\sin\chi\cos\chi\\&+\dot{\theta}\dot{\varphi}\sin\theta(\sin^2\chi-\cos^2\chi)-\dot{\varphi}^2\sin^2\theta\sin\chi\cos\chi]\\&+2xz[\dot{\theta}\dot{\varphi}\cos\theta\cos\chi+\dot{\theta}\dot{\chi}\cos\chi\\&+\dot{\varphi}^2\sin\theta\cos\theta\sin\chi+\dot{\varphi}\dot{\chi}\sin\theta\sin\chi]\\&+2yz[-\dot{\theta}\dot{\varphi}\cos\theta\sin\chi-\dot{\theta}\dot{\chi}\sin\theta\\&+\dot{\varphi}^2\sin\theta\cos\theta\cos\chi+\dot{\varphi}\dot{\chi}\sin\theta\cos\chi]. \qquad (5)\end{aligned}$$

Now let

$$\sum_{k=1}^{n} m_k(\dot{x}_k^2+\dot{y}_k^2+\dot{z}_k^2)=\sum_{i=1}^{s-3}\sum_{j=1}^{s-3} K_{ij}\dot{q}_i\dot{q}_j, \qquad (6)$$

$$\sum_{k=1}^{n} m_k(\dot{y}_k z_k-\dot{z}_k y_k)=\sum_{i=1}^{s-3} D_i\dot{q}_i,$$

$$\sum_{k=1}^{n} m_k(\dot{z}_k x_k-\dot{x}_k z_k)=\sum_{i=1}^{s-3} E_i\dot{q}_i, \qquad (7)$$

$$\sum_{k=1}^{n} m_k(\dot{x}_k y_k-\dot{y}_k x_k)=\sum_{i=1}^{s-3} F_i\dot{q}_i,$$

$$\sum_{k=1}^{n} m_k x_k^2=\{xx\}, \quad \sum_{k=1}^{n} m_k y_k^2=\{yy\},$$

$$\sum_{k=1}^{n} m_k z_k^2=\{zz\}, \quad \sum_{k=1}^{n} m_k x_k y_k=\{xy\}, \qquad (8)$$

$$\sum_{k=1}^{n} m_k x_k z_k=\{xz\}, \quad \sum_{k=1}^{n} m_k y_k z_k=\{yz\}.$$

The determinant of $2T$ can then be written; after simplification by the usual method of addition of rows or columns it becomes

$$[R]=\sin^2\theta\begin{vmatrix} K_{11} & \cdots & K_{1,\,s-3} & D_1 & E_1 & F_1 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ K_{s-3,\,1} & \cdots & K_{s-3,\,s-3} & D_{s-3} & E_{s-3} & F_{s-3} \\ D_1 & \cdots & D_{s-3} & \{yy\}+\{zz\} & -\{xy\} & -\{xz\} \\ E_1 & \cdots & E_{s-3} & -\{xy\} & \{xx\}+\{zz\} & -\{yz\} \\ F_1 & \cdots & F_{s-3} & -\{xz\} & -\{yz\} & \{xx\}+\{yy\} \end{vmatrix}. \qquad (9)$$

The integral over the external coordinates θ, φ, χ thus is always

$$\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\int_{\chi=0}^{2\pi}\sin\theta d\theta d\varphi d\chi=8\pi^2. \qquad (10)$$

The elements of the remaining determinant are functions of the internal coordinates $q_1\cdots q_{s-3}$; the completely general theory can be carried no further. The advantage of this method of treatment is that the external rotation is factored out once for all, with the result that the remaining determinant is far easier both to write and to evaluate.

Various somewhat specialized types of molecules can be defined for which a further development of the theory is possible. One such type, consisting of two tops spinning freely about an axis which is a principal axis for each, was treated by Eidinoff and Aston. Another type of wide occurrence is the pseudo-rigid molecule, consisting of a rigid framework to which any number of *symmetrical* tops are attached in any positions. This type has the property that the external moments of the molecule are independent of the internal rotations; it includes all the methyl derivatives of methane, ethylene, benzene, water, hydrogen sulfide, ammonia and formaldehyde. Many other equally simple molecules, however, such as *n*-butane, ethylamine, formic acid and phenol, fall outside the limits of this type. The further development of the general theory for these pseudo-rigid molecules is extremely simple. Take any desired X, Y, Z axes. Let the ith top have moment K_i, and the direction cosines of its axis be λ_i, μ_i, ν_i. Then in the notation already used

$$K_{ii}=K_i \quad K_{ij}=0 \text{ for } i\neq j,$$

$$D_i=\lambda_i K_i \quad E_i=\mu_i K_i \quad F_i=\nu_i K_i.$$

It follows that

$$[R]=\sin^2\theta\begin{vmatrix} K_1 & \cdots & 0 & \lambda_1K_1 & \mu_1K_1 & \nu_1K_1 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & \cdots & K_{s-3} & \lambda_{s-3}K_{s-3} & \mu_{s-3}K_{s-3} & \nu_{s-3}K_{s-3} \\ \lambda_1K_1 & \cdots & \lambda_{s-3}K_{s-3} & \{yy\}+\{zz\} & -\{xy\} & -\{xz\} \\ \mu_1K_1 & \cdots & \mu_{s-3}K_{s-3} & -\{xy\} & \{xx\}+\{zz\} & -\{yz\} \\ \nu_1K_1 & \cdots & \nu_{s-3}K_{s-3} & -\{xz\} & -\{yz\} & \{xx\}+\{yy\} \end{vmatrix}$$

$$=\sin^2\theta\prod_i K_i\begin{vmatrix} \{yy\}+\{zz\}-\{\lambda\lambda\} & -\{xy\}-\{\lambda\mu\} & -\{xz\}-\{\lambda\nu\} \\ -\{xy\}-\{\lambda\mu\} & \{xx\}+\{zz\}-\{\mu\mu\} & -\{yz\}-\{\mu\nu\} \\ -\{xz\}-\{\lambda\nu\} & -\{yz\}-\{\mu\nu\} & \{xx\}+\{yy\}-\{\nu\nu\} \end{vmatrix}, \quad (11)$$

where

$$\{\lambda\mu\}=\sum_i \lambda_i\mu_iK_i. \quad (12)$$

It is obvious that the determinant is a constant, and therefore that the integration in (2) presents no difficulty. The equation takes a strikingly symmetric form when the invariant ΣK_i is introduced.

$$[R]=\sin^2\theta\prod_i K_i\begin{vmatrix} \{yy\}+\{zz\} & & \\ +\{\mu\mu\}+\{\nu\nu\} & -\{xy\}-\{\lambda\mu\} & -\{xz\}-\{\lambda\nu\} \\ -\Sigma K_i. & & \\ & \{xx\}+\{zz\} & \\ -\{xy\}-\{\lambda\mu\} & +\{\lambda\lambda\}+\{\nu\nu\} & -\{yz\}-\{\mu\nu\} \\ & -\Sigma K_i & \\ & & \{xx\}+\{yy\} \\ -\{xz\}-\{\lambda\nu\} & -\{yz\}-\{\mu\nu\} & +\{\lambda\lambda\}+\{\mu\mu\} \\ & & -\Sigma K_i \end{vmatrix}. \quad (13)$$

There is thus an *ellipsoid of moment of inertia* which has a high formal similarity to the ellipsoid of inertia. The elements of the determinant in (13) may be called reduced moments and products of inertia, and the determinant may be considered as defining a reduced ellipsoid of inertia. Since λ, μ, ν transform under rotation of axes in exactly the same way as x, y, z, a principal axes transformation may be made here exactly as for the rigid body. For the purpose of locating the principal axes, each top of mass m_i, radius of gyration r_i, and axial direction cosines λ_i, μ_i, ν_i introduces two extra virtual mass points $m_i/2$ with coordinates λ_ir_i, μ_ir_i, ν_ir_i and $-\lambda_ir_i$, $-\mu_ir_i$, $-\nu_ir_i$. The contribution $-K_i$, that is, $-m_ir_i^2$ to each moment of inertia does not affect the location of the principal axes, but may be included in the model as a mass of $-m_i$ distributed symmetrically over the surface of a sphere of radius $(1/3)\sqrt{6}r_i$. This rigid configuration of positive and negative masses, plus the $s-3$ separate tops with axes fixed in space is thermodynamically equivalent (at high temperatures) to the pseudo-rigid molecule from which it is derived.

For most molecules of interest the symmetry is such that the principal axes of inertia coincide with the principal axes of moment of inertia and may be determined by inspection. The determinant may then be written directly in the diagonal form, with the principal reduced moments immediately apparent. For such molecules as $CH_3CH_2CD_3$ and 1,2,4-trimethylbenzene, however, this is not the case, and it might not be

obvious that there is any physically significant transformation to a diagonal determinant, or any reduced moments. The foregoing argument shows that reduced moments exist for every pseudo-rigid molecule, and thus gives a veneer of elegance to the calculation. As a matter of practical convenience, however, when at least one of the principal axes is not obvious, it is usually easier to evaluate the nondiagonal determinant in (11) than to make the frequently very cumbersome principal axes transformation of the more symmetric form (13).

It is possible that the reduced rigid molecule plus independent tops may form a useful zeroth approximation for a perturbation theory calculation of the actual energy levels of pseudo-rigid molecules. No attempt has been made to do this, however, since no application for the results is evident.

II. CH_4, C_2H_6, C_3H_8, $CH(CH_3)_3$, $C(CH_3)_4$ AND $CH_3(CH_2)_2CH_3$

Formal theory

The entire series of methylated methanes satisfy the requirements of (11), and have principal axes obvious on inspection. Ethane and tetramethylmethane have been treated previously but are included here for comparative purposes.

For ethane it must be remembered that only one methyl group is a top, the other being the rigid framework. Then, if the molecular axis is taken as the X axis, $\{yy\}=\{zz\}=K$, the moment of a methyl group, and $\lambda=1$, $\mu=\nu=0$. Hence

$$[R]=\sin^2\theta K^2(\{xx\}+K)^2. \quad \checkmark$$

The symmetry number is 18 and the rotational partition function is

$$Q_{\text{rot}}=(1/18\pi)(8\pi^3kT/h^2)^2K(\{xx\}+K),$$

as has been found previously by more laborious methods.

For propane, take the XY-plane to be that of the carbon atoms, with the Y axis bisecting the central angle. Then $\lambda_1=\sqrt{6}/3$, $\mu_1=\sqrt{3}/3$, $\nu_1=0$, $\lambda_2=-\sqrt{6}/3$, $\mu_2=\sqrt{3}/3$, $\nu_2=0$ and

$$[R]=\sin^2\theta K^2(\{xx\}+\{yy\})(\{xx\}+\{zz\}-2K/3)(\{yy\}+\{zz\}-4K/3).$$

The symmetry number is again 18 and

$$Q_{\text{rot}}=(1/18\pi)(8\pi^3kT/h^2)^{5/2}K(\{xx\}+\{yy\})^{1/2}(\{xx\}+\{zz\}-2K/3)^{1/2}\times(\{yy\}+\{zz\}-4K/3)^{1/2}.$$

For *iso*butane, take the Z axis that of the unique CH, and the XZ plane containing one CC. Then $\lambda_1=2\sqrt{2}/3$, $\mu_1=0$, $\nu_1=1/3$, $\lambda_2=-\sqrt{2}/3$, $\mu_2=\sqrt{6}/3$, $\nu_2=1/3$, $\lambda_3=\sqrt{2}/3$, $\mu_3=-\sqrt{6}/3$, $\nu_3=1/3$. Since $\{xx\}=\{yy\}$

$$[R]=\sin^2\theta K^3(\{xx\}+\{zz\}-4K/3)^2(2\{xx\}-K/3).$$

The symmetry number is 81 and

$$Q_{\text{rot}}=(1/81\pi)(8\pi^3kT/h^2)^3K^{3/2}(\{xx\}+\{zz\}-4K/3)(2\{xx\}-K/3)^{1/2}.$$

Finally, for tetramethylmethane it is merely necessary to add $\lambda_4=0$, $\mu_4=0$, $\nu_4=-1$ to the preceding case and to note that here $\{xx\}=\{yy\}=\{zz\}$. The symmetry number is $12\times81=972$. Then

$$[R]=\sin^2\theta K^4(2\{xx\}-4K/3)^3$$

and

$$Q=(1/972\pi)(8\pi^3kT/h^2)^{7/2}K^2(2\{xx\}-4K/3)^{3/2}.$$

This result is identical with that previously derived by the writer and by Eidinoff and Aston by more difficult methods.

The technique which has been developed for these calculations is thus so powerful that the longest part of the computation is the determination of the external moments, which would still be necessary if the internal rotations were frozen. If D, d are the CH and CC distances, and M, m the masses of C and H, straightforward calculation gives the following results.

Ethane $\{xx\}=MD^2/2+3mD^2/2+2mDd+2md^2/3.$

Propane
$$\{xx\}=4MD^2/3+4mD^2+8mD/3+4md^2/3$$
$$\{yy\}=(2/9+4\mu^2/9)MD^2+(1/27)(14-8\mu+32\mu^2)mD^2+4mDd/3+8md^2/3$$
$$\{zz\}=4md^2,$$

where $\mu=m/(3M+8m)$.

Isobutane
$$\{xx\}=4MD^2/3+4mD^2+8mDd/3+8md^2/3,$$
$$\{zz\}=(1/12+\mu^2/4)MD^2+(1/8)(1-2\mu+5\mu^2)mD^2+2mDd/3+14md^2/3,$$

where $\mu=m/(2M+5m)$.

Tetramethylmethane $\{xx\}=4MD^2/3+4mD^2+8mDd/3+4md^2.$

In all cases $K=8md^2/3.$

For *n*-butane the X, Y, Z axes are taken the same as in previous work on the vibrational frequencies.[4] The angle there designated φ is here called α. The angles describing the rotations of the two end methyl groups are β, γ. Then

$$\{xx\}=17MD^2/9+31mD^2/6+22mDd/9+26md^2/9,$$
$$\{yy\}=(1/9)[8(1+\mu^2)MD^2+(20-8\mu+20\mu^2)mD^2+32mDd+16md^2]\cos^2\alpha+(16/3)md^2\sin^2\alpha,$$
$$\{zz\}=(1/9)(16MD^2+48mD^2+32mDd+16md^2)\sin^2\alpha+(16/3)md^2\cos^2\alpha,$$
$$\{xy\}=0,\quad \{yz\}=0,$$
$$\{xz\}=(\sqrt{2}/9)(10MD^2+30mD^2+8mDd-8md^2)\sin\alpha,$$
$$\Sigma m(\dot{x}y-\dot{y}x)=(16\sqrt{2}/9)md^2\sin\alpha(\dot{\beta}+\dot{\gamma})=F(\dot{\beta}+\dot{\gamma}),$$
$$\Sigma m(\dot{z}x-\dot{x}z)=(\sqrt{2}/9)[(10MD^2+30mD^2+8mDd-8md^2)\dot{\alpha}-16md^2(\dot{\beta}-\dot{\gamma})]\cos\alpha=E_1\dot{\alpha}+E_2(\dot{\beta}-\dot{\gamma}),$$
$$\Sigma m(\dot{y}z-\dot{z}y)=(8/9)md^2(\dot{\beta}+\dot{\gamma})=D(\dot{\beta}+\dot{\gamma}),$$
$$\Sigma m(\dot{x}^2+\dot{y}^2+\dot{z}^2)=(1/9)\dot{\alpha}^2\{8MD^2[(1+\mu^2)+(1-\mu^2)\cos^2\alpha]+48mD^2\cos^2\alpha+mD^2(20-8\mu+20\mu^2)\sin^2\alpha+32mDd+64md^2\}+(16/9)md^2(\dot{\alpha}\dot{\beta}-\dot{\alpha}\dot{\gamma})+(8/3)md^2(\dot{\beta}^2+\dot{\gamma}^2)=K_1\dot{\alpha}^2+K_2\dot{\beta}^2+K_2\dot{\gamma}^2+2K_3(\dot{\alpha}\dot{\beta}-\dot{\alpha}\dot{\gamma}),$$

where

$$\mu=m/(2M+5m).$$

Then the determinant of $2T$ is easily written and factored, giving

$$[R]=\sin^2\theta\begin{vmatrix}K_2 & D & F\\ 2D & \{yy\}+\{zz\} & -\{xz\}\\ 2F & -\{xz\} & \{xx\}+\{yy\}\end{vmatrix}\begin{Vmatrix}K_1 & K_3 & E_1\\ 2K_3 & K_2 & 2E_2\\ E_1 & E_2 & \{xx\}+\{zz\}\end{Vmatrix}.$$

When advantage is taken of simple relationships between D, E_2, F and K_2 and between $\{xz\}$ and E_1, a further reduction is possible.

$$[R]=\sin^2\theta K_2^2[AC-(2/9)K_2C-\{(16/9)K_2A+S^2\}\sin^2\alpha]\times[K_1B-(2/9)K_2B-\{(16/9)K_2K_1+S^2\}\cos^2\alpha],\quad (14)$$

where

$$\{xx\}+\{yy\}=C,\ \{xx\}+\{zz\}=B,\ \{yy\}+\{zz\}=A,$$
$$S^2=(2/81)(10MD^2+30mD^2+8mDd-8md^2)\times(10MD^2+30mD^2+8mDd+40md^2/3).$$

Evidently $[R]$ is a function of α; hence there are no reduced moments for *n*-butane. The integration in (2) must be made by quadratures. The range of integration for each of the angles α, β, γ is 0 to 2π. The configurations α and $\alpha+\pi$ differ only in external orientation, however, and for this cause a factor 2 appears in the symmetry number. Two factors of 3 arise from the two terminal methyl groups. The end-over-end symmetry of ethane and propane is present in butane also for all values of α. The total symmetry number is therefore 36, and

$$Q_{\text{rot}}=(1/36\pi)(8\pi^3kT/h^2)^3(1/2\pi)\int_0^{2\pi}K_2(D_1D_2)^{\frac{1}{2}}d\alpha,$$

where D_1, D_2 are the two bracketed functions in (14).

Numerical values

The best values for the interatomic distances probably are $D=1.53\times10^{-8}$ cm, $d=1.11\times10^{-8}$ cm. The numerical values of the reduced moments $\times10^{40}$ are then as follows:

Methane	5.46,	5.46,	5.46,	
Ethane	41.5,	41.5,	5.46,	5.46,
Propane	109.2,	92.2,	22.44,	5.46, 5.46,
Isobutane	178.9,	98.8,	98.8,	5.46, 5.46, 5.46,
Tetramethylmethane	178.9,	178.9,	178.9,	5.46, 5.46, 5.46, 5.46.

For *n*-butane

$$(1/2\pi)\int_0^{2\pi}K_2(D_1D_2)^{\frac{1}{2}}\,d\alpha=5.957\times10^{-116}.$$

This is the effective square root of the product of the moments; it may be compared with 1.686×10^{-116} for isobutane.

[4] Kassel, J. Chem. Phys. **3**, 326 (1935).

The translational plus rotational entropies, taking account of the symmetry but omitting nuclear spin contributions are therefore

Methane	$S=-0.754+4R \log T$	$S_{298.1}=44.527$,
Ethane	$S=4.498+(9/2)R \log T$	$S_{298.1}=55.439$,
Propane	$S=9.058+5R \log T$	$S_{298.1}=65.659$,
Isobutane	$S=8.988+(11/2)R \log T$	$S_{298.1}=71.249$,
Tetramethyl-methane	$S=6.036+6R \log T$	$S_{298.1}=73.957$,
n-Butane	$S=13.105+(11/2)R \log T$	$S_{298.1}=75.366$.

The estimated vibrational entropy for *n*-butane at 298.1° is 2.79 e. u.; the value for isobutane will not differ greatly from this, so that approximate cancellation of vibrational contributions will occur. *n*-Butane is thus favored over isobutane by a ΔS of approximately 4.117 for all moderate temperatures. Heats of combustion determined by Rossini[5] indicate a ΔH of 1630 cal. favoring isobutane. An approximate value for the free energy change is then

$$n\text{-}C_4H_{10}=iso\text{-}C_4H_{10}, \quad \Delta F/T=4.117-1630/T.$$

The corresponding values of the equilibrium constant $[iso\text{-}C_4H_{10}]/[n\text{-}C_4H_{10}]$ are 1.97 at 298.1°, 0.98 at 400° and 0.65 at 500°K. The effect of the vibrational contribution is probably in the direction of still smaller equilibrium constants, especially at the higher temperatures. It is interesting to note in passing the very fair agreement of this ΔS value with the statistical third law value of 4.5 e. u. decrease per methyl group side-chain found by Parks for the liquid state.

The relatively small vibrational contributions to the entropy have been estimated on a consistent basis[6] for the four normal hydrocarbons. Table I gives these estimates, the resulting total $S_{298.1}$ values (omitting the nuclear spin contribution) and the increment per CH_2 group added in the chain. The only direct comparison with third law results is for *n*-butane, where the calculated value is 3.76 e. u. $=R$ log 6.6 higher than the experimental value of Huffman, Parks and Barmore.[7] This difference is well beyond any reasonable error in the calculation, and is presumably due either to an error in the 11.7 e. u. extrapolation from 90°K, to 0°, or to a zero-point entropy of the crystals caused by lack of equilibrium at the lower temperatures. The nearly linear increase in entropy with length of the carbon chain is of interest. The data of Parks and his associates give an increase of 7.7 e. u. per CH_2 group in the liquid state. For the hypothetical perfect gas at atmospheric pressure this would be approximately 9.3 e. u. The calculated values for longer chains will probably increase by at least 10.0 e. u. per CH_2 group.

TABLE I.

Entropies of normal hydrocarbons.

SUBSTANCE	S_{vib}	S_{total}	Δ per CH_2
Methane	0.11	44.64	
			11.32
Ethane	0.52	55.96	
			11.44
Propane	1.74	67.40	
			10.76
n-Butane	2.79	78.16	

[5] Rossini, J. Chem. Phys. **3**, 438 (1935).
[6] Using frequencies calculated by Kassel, J. Chem. Phys. **3**, 326 (1935).

III. BENZENE AND ITS ELEVEN METHYL DERIVATIVES

All these molecules consist of symmetrical tops on a rigid framework. For all except 1,2,4-trimethylbenzene the principal axes are obvious; in this one case it is readily found that the principal axes of the reduced ellipsoid of inertia make angles of 43.10° and 46.90° with the axis of the 2-methyl group. The calculations are extremely simple, requiring only a few hours for all twelve compounds. Table II gives the three reduced moments, the symmetry number, the calculated rotational plus translational entropy for the gas at 298.1°K, the experimental third law entropy for the liquid at the same temperature, and wherever possible for the gas. The interatomic distances used are[8] $d_{CC}=1.40\times10^{-8}$ cm in the benzene ring and 1.50×10^{-8} cm from the ring to the attached methyl group; $d_{CH}=1.14\times10^{-8}$ cm for hydrogen attached to the ring and 1.11×10^{-8} cm for methyl group hydrogen atoms. The third law entropies for the gaseous state are very uncertain beyond the xylenes. Even for these compounds the vapor pressure data in *International Critical Tables* are totally wrong, and the low temperature measurements of

[7] Huffman, Parks and Barmore, J. Am. Chem. Soc. **53**, 3876 (1931).
[8] Jones, Trans. Faraday Soc. **31**, 1036 (1935).

TABLE II. *Entropies of the methyl benzenes.*

SUBSTANCE	MOMENTS $\times 10^{40}$			σ'[a]	S_{t+r}	THIRD LAW S_{liq}	THIRD LAW S_{gas}
Benzene	297.22	148.61	148.61	12	59.77	41.9[b]	65.1
Toluene	477.27	328.66	148.61	2	68.72	52.4[e]	77.3
o-Xylene	638.13	383.59	254.53	2	73.76	59.3[b]	83.6
m-Xylene	693.34	466.40	226.93	2	73.92	60.3[b]	85.5
p-Xylene	720.94	572.33	148.61	4	72.37	60.5[b]	86.5
1,2,3-Trimethylbenzene	835.27	466.40	368.87	2	78.60	—	—
1,2,4-Trimethylbenzene	908.42	638.09	270.33	1	80.06	67.7[c]	94.1
1,3,5-Trimethylbenzene	932.80	466.40	466.40	6	76.76	—	—
1,2,3,4-Tetramethylbenzene	1079.2	678.26	400.90	2	83.28	69.5[c]	—
1,2,3,5-Tetramethylbenzene	1122.8	656.43	466.40	2	83.43	74.1[c]	—
1,2,4,5-Tetramethylbenzene	1144.7	784.19	360.47	4	82.00	71.8[c]	97.3
Pentamethylbenzene	1336.7	784.19	552.56	2	87.89	80.0[d]	—
Hexamethylbenzene	1568.4	784.19	784.19	12	88.74	85.5[d]	—

[a] The total symmetry number is $\sigma = 3^n\sigma'$ where n is the number of methyl groups.
[b] Huffman, Parks and Daniels, J. Am. Chem. Soc. **52**, 1547 (1930).
[c] Huffman, Parks and Barmore, J. Am. Chem. Soc. **53**, 3876 (1931).
[d] Parks, Ind. Eng. Chem. **25**, 887 (1933).
[e] Kelley, J. Am. Chem. Soc. **51**, 2740 (1929)

Linder[9] also seem to be inaccurate. The entropies of vaporization used for the xylenes in Table II have been calculated from new vapor pressure measurements which will shortly be published elsewhere. Comparison of third law gas values with theoretical translation-rotation entropies gives an indicated vibrational entropy of 9.8 e. u. for *o*-xylene and 14.1 e. u. for *p*-xylene. Either of these values might be considered plausible, but it does not seem possible that there could be such a large difference between the isomers. The vapor pressure of 1,3,5-trimethylbenzene has been measured, and the calculated entropy of vaporization has been assumed to apply to 1,2,4-trimethylbenzene. Linder's vapor pressures for 1,2,4,5-tetramethylbenzene, which presumably are for the solid, have been corrected to the liquid state by means of the same data used by Parks to estimate the entropy of fusion. For the pentamethyl and hexamethyl compounds even the liquid entropies are quite uncertain, and no attempt has been made to estimate values for the gases.

Parks concluded that the entropies of the liquid methylbenzenes could be represented by

$$S_{298.1} = 44.5 + 7.7n.$$

[9] Linder, J. Phys. Chem. **35**, 531 (1931).

The gaseous translation-rotation entropies follow a similar linear relationship considerably more closely than the experimental liquid figures do. The chief deviations arise from the varying symmetry number. The irregular part of this variation can be eliminated by adding $R\log\sigma'$. It is then found that

$$S_{t+r} + R\log\sigma' = 65.244 + 4.814n$$

represents the calculated values with a maximum deviation of 0.64 e. u. The variation is definitely nonlinear, however, and a much better representation is

$$S_{t+r} + R\log\sigma' = 64.751 + 5.406n - 0.0987n^2$$

with a maximum deviation of 0.24 e. u., and a maximum deviation of 0.066 e. u. from the average for all isomers with the same n. The maximum spread between isomers is 0.343 e. u. for the trimethylbenzenes.

The excesses of the third law values for the gases over the calculated translation-rotation entropies are of magnitudes compatible with interpretation as vibrational entropies. Any calculation of the theoretical vibrational entropies for these compounds would be premature, however, and is deferred until more complete vibrational analyses are available.

Viscosity, Plasticity, and Diffusion as Examples of Absolute Reaction Rates

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Since to form a hole the size of a molecule in a liquid requires almost the same increase in free energy as to vaporize a molecule, the concentration of vapor above the liquid is a measure of such "molecular" holes in the liquid. This provides an explanation of the law of rectilinear diameters of Cailletet and Mathias. The theory of reaction rates yields an equation for absolute viscosity applicable to cases involving activation energies where the usual theory of energy transfer does not apply. This equation reduces to a number of the successful empirical equations under the appropriate limiting conditions. The increase of viscosity with shearing stress is explained. The same theory yields an equation for the diffusion coefficient which when combined with the viscosity and applied to the results of Orr and Butler for the diffusion of heavy into light water gives a satisfactory and suggestive interpretation. The usual theories for diffusion coefficients and absolute electrical conductance should be replaced by those developed here when ion and solvent molecule are of about the same size.

INTRODUCTION

THE general equation for the rate of any process in which matter rearranges by surmounting a potential energy barrier has been proposed in the following form:[1]

$$k' = \mathfrak{C}(F_a/F_n)(\bar{p}/m^*). \tag{1}$$

Here F_a is the partition function for the activated complex per unit of length along the coordinate normal to the top of the potential barrier. The average velocity $\bar{p}/m^*$ along this coordinate must of course be expressed in these same units of length, $\bar{p}$ and m^* being the corresponding average momentum and reduced mass, respectively. F_n is the partition function for the normal state and $\mathfrak{C}$, the transmission coefficient, is the chance that a system having once crossed the potential barrier will react and not recross in the reverse direction. In (1) both partition functions are to be measured from the same zero of energy.

If the curvature normal to the barrier is sufficiently small we may treat motion in this direction as a pure translation, in which case (1) becomes:

$$k' = \mathfrak{C}\frac{F_a^*}{F_n}\frac{kT}{h}e^{-E_0/kT}. \tag{2}$$

Here F_a^* differs from F_a in two ways. First it is calculated by using a zero of energy higher by E_0 than for F_n and secondly the partition function for the degree of freedom normal to the barrier is omitted from F_a^* and included in the frequency factor kT/h. Here k, T and h are the Boltzmann constant, the absolute temperature, and the Planck constant, respectively.

The potential surface along the degree of freedom normal to the barrier is really curved and we can take account of "tunneling" up to terms involving the second power of h by multiplying (2) by the factor $(1+(1/24)(h\nu/kT)^2)$ to give

$$k' = \mathfrak{C}\frac{F_a^*}{F_n}\frac{kT}{h}\exp\left(-\frac{E_0}{kT}\right)\left(1+\frac{1}{24}\left(\frac{h\nu_n}{kT}\right)^2\right), \tag{3}$$

where $i\nu_n = (1/2\pi)(f_n/m^*)^{\frac{1}{2}}$ and f_n and m^* are the force constant and reduced mass normal to the top of the potential barrier.[2] f_n is negative. The ratio of partition functions in (2) and (3) can be written as the equilibrium constants $K = F_a/F_n$ and $K^* = F_a^* e^{-E_0/kT}/F_r$ and all the thermodynamic and statistical mechanical methods for treating or discussing any equilibrium constant are available for reaction rates.

Now if we actually calculate our potential energy surfaces and particularly if we are discussing isotope effects we may prefer to write (3) in the entirely equivalent form:

$$k' = \mathfrak{C}\left(\frac{F_a^*}{F_n}\right)_c\frac{kT}{h}\left(1+\frac{1}{24}\left(\frac{h\nu_n}{kT}\right)^2\right)\exp(-E_c/kT). \tag{4}$$

Here instead of using E_0 the actual activation energy at the absolute zero we use E_c the "classi-

[1] (a) Eyring, J. Chem. Phys. **3**, 107 (1935); (b) Evans and Polanyi, Trans. Faraday Soc. **21**, 875 (1935); (c) Wynne-Jones and Eyring, J. Chem. Phys. **3**, 492 (1935).

[2] Wigner, Zeits. f. physik. Chemie **B19**, 203 (1932).

cal activation energy at the absolute zero." This simply involves absorbing the corresponding zero point energies in the partition functions. Thus in the ratio F_a^*/F_n in (2) and (3) the partition function corresponding to the normal vibration ν_i is written as $(1-\exp(h\nu_i/kT))^{-1}$. In $(F_a^*/F_n)_c$ in (4) this same partition function is written as:

$$\left[\exp\left(-\frac{h\nu_i}{2kT}\right)\left(1-\exp\left(-\frac{h\nu_i}{kT}\right)\right)^{-1}\right] = (2\sinh h\nu_i/2kT)^{-1}.$$

There is of course no real difference between (3) and (4) and they can be used interchangeably.

Now in certain reactions such as associations of atoms and of some types of radicals there is no activation energy and, therefore, no activated state. However, when we treat the energy of rotation as a potential energy there is an activation energy and the procedure described above becomes immediately applicable.[3]

The Theory of Holes and the "Law of Rectilinear Diameters" of Cailletet and Mathias

Suppose we have N molecules forming a liquid. Then each of them is bound to the others by bonds adding up to the total energy $E=\sum_i n_i E_i$ where n_i is the number of bonds of a particular kind each of which has the bond strength E_i. To vaporize the N molecules requires an energy of exactly $NE/2$, since each bond belongs to two molecules. Therefore to vaporize a single molecule requires the energy $E/2$ providing no hole is left in the liquid. However, if we vaporize one molecule leaving the hole we must supply exactly the energy E. If we then return this gas molecule to the liquid we get back the energy $E/2$; so that it requires rigorously the same energy $E/2$ to make a hole in a liquid of a size which will just accommodate a single molecule, as it does to vaporize one molecule without leaving a hole. Stated differently it takes just the same energy for a hole the size of a molecule to detach itself from the empty space above a liquid and pass into the liquid as it does for a molecule to detach itself from the liquid and pass into the empty space. Now a molecule in empty space because it can move around freely has a considerably higher entropy than in the liquid state. That is to say it has accessible to it a large number of different states which it can assume without increasing its energy. Exactly the same is true of the hole dissolved in the liquid. A hole can take up a great many different positions in the liquid each of which has exactly the same energy. If we imagine ourselves watching these holes we would see them darting in a random fashion through the solution with a velocity characteristic of the liquid molecules at this temperature. A liquid is much like a crystal in having a more or less definite lattice arrangement. Wherever there is a hole a neighboring molecule can jump into the empty lattice point leaving a hole behind and as this process goes on continuously each hole contributes in effect a new degree of translation to the liquid. Below the critical temperature this translation in the liquid is not quite as free as in the vapor phase so that the apparent partition function to be used for the holes is somewhat smaller than for vapor molecules. At the critical temperature, however, the mobilities and therefore the two partition functions become equal. Thus for holes dissolved in liquids as for molecules dissolved in empty space we have the theorem of equal (or very nearly equal) entropies as well as energies. Now how much energy is required for the association or dissociation of holes of about molecular size depends of course upon the solvent. However, since these processes take place both in the gas and the liquid phase we assume as a first approximation that association or dissociation will not affect the distribution ratio of holes between the phases. In that case at the critical temperature we should have exactly as much matter in a cc of otherwise empty space as we have holes in a cc of matter. As we lower the temperature a plot of this average density against temperature would almost parallel the temperature axis, the density increasing slightly as the temperature decreases. Thus the average density of the vapor and liquid phase should to this approximation be nearly independent of the vapor pressure (or the temperature). Now the law of rectilinear diameters states that for actual cases such a plot of average

[3] Eyring, Gershinowitz and Sun, J. Chem. Phys. **3**, 786 (1935).

density is a straight line but that it may and in general is somewhat inclined with respect to the temperature axis. Thus the law of Cailletet and Mathias follows from the statistical mechanical consideration of holes.

The theorem of equal energy, and approximately equal entropy for holes in matter as for molecules in empty space frequently applies in the same way to solids as to liquids, and the concentration of the vapor is then a rough measure of the number of holes in the condensed phase. Polarization forces necessitate modification of this idea of equal energy in some solids as Schottky has pointed out.[4]

The theory of holes is important for all phenomena in which a part of the matter in a condensed phase moves with respect to other parts, since at the borders of holes such motions can be set up with a minimum of disturbance to molecules not participating in the motion. In certain phenomena it may be simpler to fix attention on the few holes than the much more numerous molecules. Thus in the melting of crystals the disorder which must set in by one group of molecules first moving with respect to a second group and so releasing the latter from a part of their restraining potential (this in turn releasing a third group, etc.) may begin at a hole. More probably, however, it will begin at a crystal boundary since the heat is ordinarily supplied there. If the melting involves expansion then small holes will not permit the melting to go far just as reactions involving expansions cannot take place except at an interface. Sharp melting points only occur in well ordered crystals, not for example in glasses. This is as we would expect since only in very precisely ordered arrangements can the attainment of a critical motion by a few molecules profoundly affect the stability of neighbors and these in turn release still others from their restraining potential. The problem of order-disorder has been discussed at length by Bragg and Williams,[5] by Fowler and others.[6]

Some support for the general point of view with respect to holes as developed here may be obtained from discussions of the Wilson theory of semiconductors. In this theory electrical conductance is assumed to arise from thermal fluctuations which raise an electron of low energy up to the conduction levels leaving a positive hole behind. The theory seems to account satisfactorily for the observed facts.[7] We now proceed to develop a theory of viscosity in condensed phases from the point of view of absolute reaction rates.

Viscosity

The perpendicular distance between two neighboring layers of molecules sliding past each other is taken as λ_1. The motion is assumed to take place by an individual molecule in a plane (or layer) occasionally acquiring the activation energy necessary to slip over the potential barrier (arising from squeezing against its neighbors) to the next equilibrium position in this same plane. The average distance between these equilibrium positions in the direction of motion is taken as λ while the distance between neighboring molecules in this same direction is λ_2 which may or may not equal λ. The molecule to molecule distance in the plane normal to the direction of motion is written as λ_3. By definition we have for the viscosity $\eta = f\lambda_1/\Delta V$. Here f is the force per square centimeter tending to displace one layer with respect to the other and ΔV is the difference in velocity of these two layers which are a distance λ_1 apart. Now the number of times that a molecule moves in the forward direction in a second may be written as the corresponding specific reaction rate

$$k_f = \mathfrak{C}\frac{F_a^*}{F_n}\frac{kT}{h}\left(1+\frac{1}{24}\left(\frac{h\nu_i}{kT}\right)^2\right)$$
$$\exp\left(-\frac{(E_0-\frac{1}{2}f\lambda_2\lambda_3\lambda)}{kT}\right) = k_1 \exp\frac{f\lambda_2\lambda_3\lambda}{2kT}, \quad (5)$$

Here k_1 is the absolute rate for the transition (see Eq. (3)) when no force is applied. The significance of the term $\exp f\lambda_2\lambda_3\lambda/2kT$ may be seen as follows. The force acting on a single molecule is clearly $f\lambda_2\lambda_3$ and it acts to lessen the work of passing over the barrier through a distance $\lambda/2$;

[4] Schottky, Zeits. f. physik. Chemie **B29**, 335 (1935).
[5] Bragg and Williams, Proc. Roy. Soc. **A145**, 699 (1934).
[6] Fowler, Proc. Roy. Soc. **A151**, 1 (1935); Mott, Proc. Roy. Soc. **A146**, 465 (1934).
[7] Fowler, Proc. Roy. Soc. **A140**, 505 (1933); Frenkel, Todes and Ismailow, Acta Physicochimica U.S.S.R. **1**, 97 (1934).

so that in this forward direction the height of the barrier is in effect lowered by the amount $f\lambda_2\lambda_3\lambda/2$ while in the backward direction it is raised by the same amount. Thus for the backward direction we have $k_b=k_1\exp(-f\lambda_2\lambda_3\lambda/2)$. Now ΔV for each molecule in the fast layer and therefore for the layer as a whole is then just:

$$\Delta V=\lambda k_1\left(\exp\frac{f\lambda_2\lambda_3\lambda}{2kT}-\exp\left(-\frac{f\lambda_2\lambda_3\lambda}{2kT}\right)\right) \quad (6)$$

or
$$\Delta V=\lambda k_1 2\sinh(f\lambda_2\lambda_3\lambda/2kT). \quad (7)$$

So that

$$\eta=f\lambda_1\left(\lambda k_1\exp\left(\frac{f\lambda_2\lambda_3\lambda}{2kT}\right)-\exp\left(\frac{-f\lambda_2\lambda_3\lambda}{2kT}\right)\right)^{-1}$$

$$=\lambda_1 f(\lambda k_1 2\sinh(f\lambda_2\lambda_3\lambda/2kT))^{-1}. \quad (8)$$

Now for ordinary viscous flow $f\lambda_2\lambda_3\lambda/2\ll kT$ so that expanding the exponentials and keeping terms only up to the first power we have after cancelation

$$\eta=\lambda_1 kT(\lambda^2\lambda_2\lambda_3 k_1)^{-1}. \quad (9)$$

Now if we substitute our explicit expression for this frequency k_1 we obtain:

$$\eta=(\lambda_1 hF_n/\lambda^2\lambda_2\lambda_3 F_a{}^*\mathfrak{C})\exp(E_0/kT). \quad (10)$$

Since viscous flow is a rate process we know it will proceed by all possible mechanisms but chiefly by the fastest ones. Thus those orientations of the molecules are favored which lessen the viscosity. First in importance: a molecule in the activated state will be oriented in such a way as to make the activation energy E_0 as small as possible in spite of the fact that such a requirement of nearly exact orientation tends to make $F_a{}^*$ smaller and therefore $F_n/F_a{}^*$ larger. Other things being equal then E_0 will tend to be small and $\lambda^2\lambda_2\lambda_3/\lambda_1$ large. $\mathfrak{C}$, the chance that after a system has once reached the activated configuration it will pass over the barrier and not immediately return to the initial configuration, is probably very nearly unity. Thus from (10) we see that a molecule like benzene will tend to have its plane in the plane of the layer as it passes through the activated configuration as this will make λ_1 and E_0 smaller and $\lambda^2\lambda_2\lambda_3$ larger. Now a molecule is oriented in this way (k_f+k_b) times per second so that if τ_R is its relaxation time through rotation after orientation the fraction of the time it is thus oriented will be approximately

$$a=(k_f+k_b)\tau_R \quad (11)$$

as long as a is considerably less than 1. Since (k_f+k_b) can be determined from the measured viscosity either τ_R or a follows from a knowledge of the other. Since relaxation by rotation will in general involve the passage over a potential energy barrier we can write $\tau_R=1/k_2$ where k_2 is the k' of Eq. (3) after an appropriate assignment of values for the quantities therein. A good approximation for such rotations in most cases will be

$$1/\tau_R=k_2=(kT/h)\exp(-E_0/kT) \quad (12)$$

where the activation energy is the only unknown. If E_0 is negligibly small $\tau_R\approx h/kT\approx 2\times10^{-13}$ sec. around room temperature. However, there are cases such as the orientation of the dipoles of water in an alternating field near the melting point where these dipoles seem unable to follow the field for frequencies in excess of 60,000 cycles.[8] Substituting this number for k_2' in (12) we find that this relaxation must involve passage over a barrier of about 10 kcal. Hysteresis effects and relaxation processes are in general simply reaction processes to be treated by Eqs. (3) or in the simpler cases by (12).[8a] One can of course regard k_1, k_f, k_b in our viscosity equations as the reciprocals of the various relaxation times required for vibration to change into translation.

Comparison of the Theory of Viscosity for Liquids and Gases

For the viscosity theory to apply as we have developed it the following condition must be fulfilled. A molecule after making the jump from one minimum to the next must remain in the new minimum long enough to dissipate the energy it possessed while passing over the last barrier. Thus at each minimum it must acquire anew the activation energy as a purely random process. When these conditions are not fulfilled we can

[8] Smyth and Hitchcock, J. Am. Chem. Soc. **54**, 4631 (1932).

[8a] In this sense even very large relaxation times have physical significance and may be employed serviceably in the interpretation of liquid-vitreous and vitreous-crystal transitions as Professor W. T. Richards points out in a paper soon to be published.

more appropriately assume the usual mechanism of transfer of momentum from one layer to the next by the molecules themselves passing back and forth between fast and slow layers. In this case the momentum transferred per square centimeter per second is readily seen to be $\eta dv/dz = \frac{1}{3}\nu\bar{c}ml dv/dz$; so that

$$\eta = \tfrac{1}{3}\nu\bar{c}ml. \tag{13}$$

Here dv/dz, ν, $\bar{c}$, m and l are the velocity gradient, molecules per cc, mean velocity of the molecules ($\bar{c}=2(2kT/\pi m)^{\frac{1}{2}}$), mass and mean free path, respectively. Clearly (10) will apply if the activation energy for the forward direction ($E_0 - f\lambda_2\lambda_3\lambda/2$) is equal to or greater than about twice kT since then the molecule will have a sufficient number of collisions with neighbors in between passages over successive barriers so that equilibrium statistics will apply. The equation should still apply approximately even for cases where the activation energy drops to kT. It is of some interest to see how (10) compares formally with (13) if we apply the former arbitrarily to liquids or gases not showing an activation energy. In that case η takes the form

$$\eta = \frac{\lambda_1 h}{\mathfrak{C}\lambda^2\lambda_2\lambda_3}\frac{F_n}{F_a^*} \approx \frac{\lambda_1 h}{\mathfrak{C}\lambda^2\lambda_2\lambda_3}\frac{(2\pi mkT)^{\frac{1}{2}}\lambda}{h}$$

$$\approx (2\pi mkT)^{\frac{1}{2}}/\lambda^2. \tag{14}$$

Here we have assumed that the λ's become equal to each other, $E_0 = 0$, and

$$F_n/F_a^* = (2\pi mkT)^{\frac{1}{2}}\lambda/h \tag{15}$$

and of course $\mathfrak{C}=1$. Comparing this with Eq. (13) after substituting the value for $\bar{c}$ we find that the two mechanisms lead to the same result only if we make the identification

$$l\lambda^2 = (1/\nu)(3\pi/2). \tag{16}$$

In the case of liquids without activation energy we might very well take (16) as a defining equation for l or λ^2. In any case any reasonable way of arriving at λ^2 will lead to satisfactory values for λ in this critical region of activation energies where neither the reaction theory of viscosities (Eq. (10)) nor the momentum transfer theory (Eq. (13)) strictly applies. An exactly parallel situation arises in "unimolecular" reactions where at high pressure the slow (rate determining) process is passage over the potential barrier (inside a molecule) while at very low pressures the rate determining process becomes the rate at which energy is supplied by collisions. In the theory of viscosity it may be possible to bridge the intermediate region by the same type of treatment used for reaction rates. We shall not, however, develop this part of the theory further here.

Andrade[9] has proposed applying the momentum transfer theory to liquids as well as gases. He modifies the gas treatment by taking account of the fact that energy transfer in liquids is due to vibrations instead of translations. For the metals he secures excellent numerical agreement with experiment by a reasonable choice of the quantities entering into his equation. It is just these cases for which gas-like transfer is to be expected since $(E - f\lambda_2\lambda_3\lambda^2/2)(kT)^{-1}$ is very small. On the other hand where this exponential factor is not very small we must adopt the reaction rate picture for viscosity which leads us to Eq. (10).

Comparison of the Viscosity Equation with Experiment

In the second paper Andrade has proposed an equation $\eta = (A/v^{\frac{1}{3}})\exp(c/vT)$ where A and c are parameters left undetermined; v is the specific volume and T the temperature. He has then determined A and c for a wide variety of substances using the available experimental values for η over a temperature range and assembled the results in his Table IV which we need not reproduce. The present theory supplies these parameters only if we can calculate the difference in energy for the initial and the activated configurations as well as the corresponding vibrational frequencies and moments of inertia. To do this exactly we would have to treat the whole liquid mechanically as though it were a single molecule. Fortunately in the ratio of partition functions F_n/F_a^* of (10) all degrees of freedom which are unchanged in the initial and final states disappear and the same is of course true with regard to the energy term E_0. Further, any process involving a large E_0 will be of negligible importance compared with those having smaller

[9] Andrade, Phil. Mag. **17**, 497, 698 (1934).

energies. The result of this is that for the important rate processes only a very few degrees of freedom will be modified—more profound changes being excluded by the Boltzmann factor. In chemical reactions this is exemplified by the existence of type reactions which remain almost unchanged by profound changes in the molecule at distances two or three atoms away from the seat of reaction. This fact is of fundamental importance for the general mechanical approach to rate processes. Here it means that for ordinary viscous flow we shall expect the layers to slip over each other by one molecule at a time slipping past the surrounding molecules into a small hole. It would be unnaturally extravagant of energy to provide a hole the size of a molecule.

The partition function F_n for the normal state contains one more degree of freedom than F_a^* for the activated state. The simplest assumption then is that all but this one degree of freedom cancels out in the ratio of partition functions and that

$$F_n/F_a^* = (1-\exp -h\nu_i/kT)^{-1}, \qquad (17)$$

where ν_i is a vibration which can be estimated from the specific heat of the liquid. The existence of an activation energy for flow is the best possible justification for treating this additional degree of freedom in F_n as a vibration rather than a translation. In some cases ν_i may be fairly large in which case $F_n/F_a^* \approx 1$. By trying this latter approximation for this ratio and taking the transmission coefficient $\mathfrak{K}=1$ (which must in general be a very good approximation) (10) becomes:

$$\eta = (\lambda_1 h/\lambda^2\lambda_2\lambda_3)\exp(E_0/kT). \qquad (18)$$

If the distance λ between minima for the moving molecule is taken equal to λ_1, the distance between layers, we get finally that

$$\eta = (Nh/V)\exp(E_0/kT), \qquad (19)$$

where N is Avogadro's number and V is the molal volume. Now if for the molal volume we take as a rough average value $V=39.6$ cc in order to get (19) in round numbers we obtain

$$\eta = 10^{-4}\exp E_0/kT). \qquad (19)$$

The constant factor 10^{-4} is about one-quarter to one-fifth of Andrade's values for about seventy of his hundred odd examples. Now the factor (17) which has been neglected is necessarily greater than 1 and at $T=300°$ absolute it becomes equal to 4 and 5 for the respective values 1.8×10^{12} and 1.4×10^{12} for ν_i. This is about the values for the frequencies which Lindemann's theory for melting leads to. These frequencies can also be estimated from the vapor pressures of the liquids and from the specific heat c_v if we assume the expression $(1-\exp -h\nu_i/kT)^{-3}$ for the three "translational" degrees of freedom. The values obtained in this way are also of about the right size to account for these properties.

Thus for nonassociated liquids the formula

$$\eta = \frac{Nh\exp(E_0/kT)}{V\left(1-\exp\left(-\frac{h\nu_i}{kT}\right)\right)} \qquad (20)$$

seems satisfactory where ν_i can be chosen to fit the viscosity at a particular temperature or estimated from some other property as mentioned above. Instead of treating this partition function as a vibration we can, of course, treat the liquid molecule as though it were moving in a box of length d where we can think of d^3 as the "free space" per molecule. In this way we get

$$F_n/F_a^* = (2\pi mkT)^{\frac{1}{2}}d/h \qquad (21)$$

and

$$\eta = (Nd/V)(2\pi mkT)^{\frac{1}{2}}\exp(E_0/kT). \qquad (22)$$

Again reasonable values for d give agreement with experiment. The cases which do not agree with (20) and (22) fall into two categories. First those in which the activation energy is very small so that the condition that the molecule remains in a minimum long enough to dissipate and then reacquire the activation energy before continuing the journey is not fulfilled. These, however, are the cases to which the momentum transfer theory as developed by Andrade apply. The other examples are those which Andrade classifies as associated. Here he gets lower values for this constant. That this should be so follows immediately from (10) since F_n the partition function for the normal state is decreased by association more than F_a^*, and the activation process will now involve dissociation with a correspondingly high activation energy. This is another example of the general phenomenon in reaction rates that with an abnormally high E_0 there is in general

associated an abnormally high F_a^*/F_n. The reason is that the large E_0 arises from loosening an abnormally large number of bonds (or from loosening very strong bonds) and this automatically means a large value for the ratio F_a^*/F_n. This same situation is familiar in equilibrium processes.

Comparison with Other Equations

We now consider the value of E_0. The energy required to provide a hole in the liquid has already been related to the vapor pressure and this as well as the energy for an atom to pass over the energy barrier is, of course, related to the internal energy plus the energy required to overcome the external pressure. Following Andrade and Bridgman[10] we assume it is at least approximately of the form $E_0=(p+a/v^2)s$ where we write van der Waals equation as $(p+a/v^2)\times(v-b)=RT$, s is of course a volume, and the other quantities have their usual meaning. Substituting in (19) we have

$$\eta=\frac{Nh\exp\dfrac{(p+a/v^2)\,s}{RT}}{V\left(1-\exp\left(-\dfrac{h\nu_i}{kT}\right)\right)}=\frac{Nh\exp\dfrac{s}{V-b}}{V\left(1-\exp\left(-\dfrac{h\nu_i}{kT}\right)\right)}. \quad (23)$$

Now not too far below the critical temperature where $s/(V-b)$ is small we can write

$$\exp\frac{s}{V-b}=1+\frac{s}{V-b}=\frac{V-b+s}{V-b}$$

and

$$\eta=\frac{Nh(V-b-s)}{V(1-\exp-(h\nu_i/kT))}\,\frac{1}{V-b}\approx\frac{c'}{V-b}. \quad (24)$$

Batschinski[11] proposed an equation of just the form of (24) where c' is a constant. As a matter of fact he used the specific volume as we can do also by simply dividing numerator and denominator by the molecular weight. He obtained very good agreement with experiment for all nonassociated compounds. Inspection of Andrade's Table IV indicates that the ratio $s/(V-b)$ in Eq. (23) should be in the neighborhood of two or three for most of the substances provided they are nonassociated and are not too near the critical temperature. Now from experiment as well as from the theory of holes $V-b$ is about half the critical volume, V_c, at temperatures corresponding to low vapor pressures and $b=V_c/3$; so that if s is taken equal to b we have $s/(V-b)=b/(V-b)\approx 2$. In other words for nonassociated liquids E_0/kT is approximately the volume, b, occupied by the molecules themselves divided by the volume occupied by the holes, $V-b$. This last interpretation in spite of its attractiveness should not be taken too seriously, however, since b of van der Waals' equation has no very precise meaning in terms of molecular structure and is much smaller than we would deduce for example by equating $V-b$, the volume occupied by holes in the liquid, to the volume occupied by the molecules themselves in the vapor phase. This last comparison is suggested by the theory of holes.

It is interesting to compare (9) with Maxwell's equation[12] for viscosity $\eta=\epsilon\tau$ where ϵ is the elasticity and τ is the relaxation time. Doing this gives the equalities $\tau=1/k_1$ and $\epsilon=\lambda_1 kT/\lambda^2\lambda_2\lambda_3\approx kT/\lambda^3$. Thus we see that Maxwell's elasticity can be thought of as the pressure exerted by a molecule restricted to its actual volume in the liquid if it obeyed the perfect gas law.

Plasticity and the Behavior of Viscosity for Large Shearing Forces

From Eq. (8) we see that viscosity is independent of the shear only when the work done by the applied force in carrying a molecule over the barrier is small compared with kT. In cases where a fairly rigid structure is being disrupted as for example in certain gels[13] and in glasses or crystals (8) must be used instead of (10). Expanding $\sinh(f\lambda_2\lambda_3\lambda/2kT)$ in (8) and dividing the f out we obtain

[10] Bridgman, *The Physics of High Pressure* (Macmillan), p. 356.

[11] Batschinski, Zeits. f. physik. Chemie **84**, 643 (1913). See also Hatschek, *The Viscosity of Liquids* (G. Bell & Sons), Chapter V.

[12] J. C. Maxwell, Phil. Mag. **35**, 133 (1868).

[13] Hatschek, *The Viscosity of Liquids*, Chapter XII.

$$\eta=\frac{\lambda_1 kT}{\lambda^2 k_1\lambda_2\lambda_3}\left(1+\frac{1}{6}\left(\frac{f\lambda_2\lambda_3\lambda}{2kT}\right)^2 + \frac{1}{120}\left(\frac{f\lambda_2\lambda_3\lambda}{2kT}\right)^4+\cdots\right)^{-1}, \quad (24)$$

which is the limiting viscosity for zero force divided by a sum of even powers of $f\lambda_2\lambda_3\lambda/2kT$. (24) explains the generally observed fact that the viscosity decreases with the shearing force. This decrease might be expected to manifest itself particularly strongly in colloidal solutions which are inhomogeneous since then the stress concentrates on the resisting structure and the work $f\lambda\lambda_2\lambda_3/2$ done in surmounting a potential barrier may approach or even exceed kT in magnitude.

In cases where $f\lambda\lambda_2\lambda_3/2 \gg kT$ we may even neglect k_b in comparison with k_f in which case we can write (8) in the form:

$$\eta=f\lambda_1(\lambda k_f)^{-1}. \quad (25)$$

Let us now consider the rate of release of the strain f in a glass at a temperature below the softening point. If to release the strain each molecule must on the average surmount m barriers and if the average time, t, to surmount a barrier is the relaxation time $\tau=1/k_f$ then:

$$\frac{df}{dt}=\frac{f}{m\tau}=\frac{fk_f}{m}=\frac{f^2\lambda_1}{m\lambda\eta}. \quad (26)$$

This dependence of the time derivative on the square of the stress for glass has been observed by Adams and Williamson.[14] Hampton[15] has determined experimentally that the constant which we have written as $\lambda_1/m\lambda$ in (26) has the value 1000 for glass if the measured viscosity η for flow is used. This factor might arise in several ways. First, for example, the release of stress may proceed by some other relaxation than flow so that a different relaxation time (or viscosity) say that for rotation should be used. This still would give the same dependence on force squared but in that case a different η should be used. A second possibility is that the strain in the glass is such that the gth layer (each of thickness λ_1) normal to the planes of flow is strained a distance λ with respect to the first layer along the direction of flow. This strain can then be released by a displacement of an amount λ of any one of the g molecules lying in the direction in which λ_1 is measured or by an average displacement of $m=1/g$ of all of them. If g equals a thousand or more precisely if $\lambda_1/m\lambda=1000$ we obtain Hampton's result. Thirdly this same average relaxation time of $\tau/1000$ would be obtained if in the cooled glass a thousand molecules jump together with the same relaxation time that one jumped under the circumstances for which η was measured. The fact that quite generally solids have only about 1/1000 the tensile strength that might be expected theoretically has been explained as due to the fact that large groups of atoms move together with no more shearing force than would be expected for one. Polanyi[16] has pointed out that if due to strain the first and $(n+1)$st atom in one row coincides with the first and nth in a second row where in each row they are uniformly spaced then one group can be displaced with respect to the other with $1/n$th the energy required when the n atoms in one layer coincide with n in the other. In any case the law $df/dt=$constant f^2/η is to be expected whenever the stress is large.

When the stress is small we expect

$$df/dt=f/\tau=fk_1=\lambda_1 kTf/\lambda^2\lambda_2\lambda_3\eta. \quad (27)$$

Here we have used (9) to determine the relaxation time $\tau=1/k_1$. Hence for small stresses df/dt = constant f/η. Some cases will no doubt approximate the two extremes while others will be intermediate. The absolute reaction rate theory thus seems to give a very satisfactory account of viscosity and plasticity. For the latter it yields relations at least very similar to those of Prandtl, Becker, Orowan, G. I. Taylor and Polanyi as presented in their papers and which W. G. and J. M. Burgers[17] have summarized along with their own ideas in a recent report on elasticity and plasticity. Hysteresis and polymorphic transformations like any other reactions can be treated by the general theory but in each case we must secure the potential energy surface or the equivalent in other information.

[14] Adams and Williamson, J. Frank. Inst. **190**, 619 (1920); Adams, ibid. **216**, 39 (1933).

[15] Hampton, Trans. Opt. Soc. London **27**, 173 (1925–1926).

[16] Polanyi, Zeits. f. Physik **89**, 660 (1935).

[17] W. G. Burgers and J. M. Burgers. Verh. Akad. Amsterdam (1) **15**, Chapter V (1935).

Diffusion

We assume the concentration gradient is in the x direction and is equal to dc_1/dx and further that the distance between two successive minima for the diffusing molecules is λ. Then if the concentration at one minimum is c_1 that at the next minimum in the positive direction is $c_1+\lambda dc_1/dx$. Now the number of molecules of type one passing through the y, z plane per square centimeter in the positive x direction is $N\lambda k_1 c_1$ and in the reverse direction $N\lambda k_1(c_1+dc_1/dx)$. The excess proceeding in the negative x direction is $DNdc_1/dx = N\lambda^2 k_1 dc_1/dx$. Thus the diffusion coefficient is

$$D=\lambda^2 k_1 \tag{28}$$

N is again Avogadro's number and the other quantities have also been defined. The net flow in one direction of molecules of one kind is of course compensated for by the corresponding flow in the reverse direction of other types of molecules. This treatment only applies when the molecules are of approximately the same size. If for example one type of molecule is very much larger than the other it is customary to assume that the large molecules behave like very large balls around which the smaller molecules stream. Then Stokes[18] equation $\dot{x}=X/6\pi r\eta$ applies to the large molecules where $\dot{x}$, r and X are the velocity, radius and force acting on one of them and η is the viscosity of the small ones. The osmotic force acting on the large molecule is $X=-V\times(dc/dx)NkT$; so that the excess of large molecules passing in the positive x direction per cm^2 per second is

$$\frac{\dot{x}}{V}=-\frac{kT}{6\pi r\eta}\frac{dc_1}{dx}N=-D\frac{dc_1}{dx}N, \tag{29}$$

which gives the well-known relationship

$$D=kT/6\pi r\eta. \tag{30}$$

The definition of all the quantities is the same used previously where c_1 is the concentration of the large molecules in moles per cc and V is the reciprocal of the number of these large molecules per cc.

On the other hand for molecules of the same size where (9) and (28) apply we obtain:

$$D=\lambda_1 kT/\lambda_2\lambda_3\eta. \tag{31}$$

Thus (30) and (31) each have a well-defined region in which they do and do not apply. There is an intermediate region which requires closer consideration, and which we hope to consider further at another time. We now apply (31) to the diffusion of heavy into light water. Orr and Butler[19] give for this diffusion coefficient 1.46×10^{-5} at 0°C and 4.75×10^{-5} at 45°C. The viscosities at these two temperatures given by Landolt-Börnstein are 0.0179 and 0.00667, respectively. Substituting in (31) we obtain for $\lambda_2\lambda_3/\lambda_1$ at 0° the value 1.43×10^{-7} and at 45°C the value 1.38×10^{-7} cm. Now the geometrical mean of the λ's is $(\lambda_1\lambda_2\lambda_3)^{\frac{1}{3}}=(18/N)^{\frac{1}{3}}=3.1\times10^{-8}$ cm. Combining these values we find that at 45°, $\lambda_1=1.47\times10^{-8}$ and $(\lambda_2\lambda_3)^{\frac{1}{2}}=4.50\times10^{-8}$ cm, while the values for zero degrees give $\lambda_1=1.44\times10^{-8}$ and $(\lambda_2\lambda_3)^{\frac{1}{2}}=4.54\times10^{-8}$ cm. This is precisely the kind of result that would be predicted since from general principles we expected that in viscous flow the plane of the H_2O molecule would tend to coincide with a plane of flow, i.e., that λ_1 would be the thin dimension of H_2O. In our calculation we have used the viscosity of H_2O whereas we should have used a value intermediate between that of H_2O and the value for pure D_2O which is about 30 percent higher than the former. Such a correction would decrease somewhat the ratio $(\lambda_2\lambda_3)^{\frac{1}{2}}\lambda_1^{-1}$ but would leave our general result unchanged. Thus we apparently have a very suggestive check of the theory. Eq. (30) on the other hand leads to the unreasonably small values for $2r$ of 1.46×10^{-8} cm at 45° and 1.56×10^{-8} cm at 0°C.

In electrical conductance the use of (30) for the diffusion coefficient certainly tends to give too low results for ionic mobility and is only justified if the ions are very much solvated or for other reasons very large as compared with the solvent. If the ions are of the same size as the solvent we should use (31) and in any case for large potential gradients we should use η in the form (8) or (24) where f is now the force acting on the ion due to the applied potential modified of course in the usual way by the other charges.

I want to thank Mr. R. H. Ewell for calling my attention to the interesting nature of the problem of viscosity.

[18] C.f. Herzfeld, *Kinetische Theory der Wärme* (Müller-Pouillets Lehrbuch der physik., 1925), Chapter VII.

[19] Orr and Butler, J. Chem. Soc. 1273 (1935).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Absolute Rate of Reactions in Condensed Phases.[1] A Criticism

In the treatment of bimolecular reactions in solution, which forms the bulk of a recent publication by Wynne-Jones and Eyring[1] there appear two errors. It is the object of this letter to disclose them, and to show how their accidental cancelation has led to "entropy" values which, while possessing no physical significance, have escaped the fantastic magnitudes which they would have had if only one of the errors had been committed.

Omitting the transmission coefficient, κ, which is always assumed to be unity, the expression for the specific reaction rate is written

$$k' = e^{-\Delta H^{\ddagger}/RT} \cdot e^{\Delta S/R} kT/h. \tag{1}$$

Combining this equation with the experimental relation

$$k' = Z \cdot e^{-E/RT} \tag{2}$$

enables Wynne-Jones and Eyring to calculate the "entropy of activation." We have repeated the calculations, and find values in substantial agreement, as shown by the results in Table I. Where small differences appear, they are due to the fact that we have calculated the results for specified temperatures at which the experiments were performed. The agreement, however, has been made possible only by following their steps closely, and thereby ignoring the facts that Eq. (1) is dimensionally incorrect, and that Eq. (2) gives results in the experimental units of liters per mole-second, rather than in the theoretical units of cc per molecule-second.

Eq. (1) is based on the following expression given by Wynne-Jones and Eyring for the equilibrium constant governing the formation of the complex;—

$$K^{\ddagger} = e^{-\Delta H^{\ddagger}/RT} \cdot e^{\Delta S/R}. \tag{3}$$

TABLE I.

REACTION	SOLVENT	T	Z	$-\Delta S^{\ddagger}$ (W-J. & E.)	$-\Delta S^{\ddagger}$ (recalc.)
$NH_4^+ + CNO^-$	H_2O	326	4.27×10^{12}	0.9	0.9
$(CH_3)_2CO + C_2H_5COOH$	H_2O	298	1.12×10^{7}	26.7	26.3
$CH_3I + C_6H_5N(CH_3)_2$	$C_6H_5NO_2$	303	2.47×10^{4}	37.5	38.5
$C_2H_5Br + (C_2H_5)_3N$	C_6H_6	331	1.47×10^{2}	48.1	48.8

This expression is dimensionless, and is inconsistent with the other expressions

$$K^{\ddagger} = \frac{c^{\ddagger}}{c_1 c_2 \cdots c_i} \cdot \frac{\alpha^{\ddagger}}{\alpha_1 \alpha_2 \cdots \alpha_i} \tag{4}$$

and

$$K^{\ddagger} = (F_a'/F_n) \cdot e^{-E_0/kT} \tag{5}$$

which are also quoted in the paper, and which give (correctly) the equilibrium constant in terms of activities and of partition functions respectively. The satisfactory ad justment of Eq. (3) requires that we multiply the expression on the right-hand side by a volume term. A little consideration will show that, if we multiply it by the volume occupied by the complex (which we shall call $(4/3)\pi r^3$), the equation becomes dimensionally correct, and gives numerically the equilibrium constant in cc per molecule:

$$K^{\ddagger} = (4/3)\pi r^3 \cdot e^{-\Delta H^{\ddagger}/RT} \cdot e^{\Delta S/R}. \tag{3a}$$

Hence, to express the bimolecular velocity constant in cc per molecule-second, we must multiply Eq. (1) also by $(4/3)\pi r^3$;

$$k' = (4/3)\pi r^3 \cdot e^{-\Delta H^{\ddagger}/RT} \cdot e^{\Delta S/R} \cdot kT/h. \tag{1a}$$

To convert the experimental Eq. (2) into the same units, we must introduce the factor $1000/N_0$, where N_0 is the Avogadro number;

$$k' = (1000/N_0) \cdot Z \cdot e^{-E/RT}. \tag{2a}$$

The apparent success attending the theory of Wynne-Jones and Eyring is thus due to the circumstance that the ratio $(4/3)\pi r^3/1000/N_0$ is of the order of magnitude 1 for rational values of r. To make the ratio exactly 1, r would have to be 7.33A. While this circumstance explains the order of magnitude of the "entropy" values calculated by Wynne-Jones and Eyring, it can confer no validity on their theory, which is fundamentally spurious.

E. A. MOELWYN-HUGHES

University Chemical Laboratory,
Cambridge, England,
October 5, 1935.

[1] W. F. K. Wynne-Jones and Henry Eyring, J. Chem. Phys. 3, 492 (1935).

Answer to a Criticism by Moelwyn-Hughes of a Paper by Wynne-Jones and Eyring

The preceding criticism by Moelwyn-Hughes is without foundation. In defining the entropy of activation a standard state must be chosen. We chose as our standard concentration the same unit concentration used in defining the experimental reaction rate k_{exp}. We indicated this explicitly by our Eq. (4)

$$k_{exp} = \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right)\exp\left(\frac{\Delta S^{\ddagger}}{R}\right)\cdot\frac{kT}{h}$$

from which we calculate $\Delta S^{\ddagger}$. This choice of the concentration of the standard state was made to avoid the volume factor

$$(V/V^{\ddagger})^{n-1} = e^{R \ln (V/V^{\ddagger})^{n-1}/R} \qquad (5)$$

on the right side of (4) which must be included if we choose different standard concentrations for k_{exp} and for $\Delta S^{\ddagger}$. Here $V/V^{\ddagger}$ is the volume containing a mole at the standard concentration for k_{exp}, divided by the volume containing a mole at the standard state chosen for $\Delta S^{\ddagger}$. By choosing as our standard concentration for defining $\Delta S^{\ddagger}$ the same standard concentration used for k_{exp} the factor $V/V^{\ddagger}$ thus becomes unity and disappears from our equation (see (4)). n is the order of the reaction. Having adopted this convention for $\Delta S^{\ddagger}$ if we now wish to compare it with the change in entropy, ΔS, for some equilibrium in which the standard volume containing a mole is V we must (as we in fact did) first add to ΔS the term $R \ln (V/V^{\ddagger})^{n-1}$. If Moelwyn-Hughes does not like this convention that is of course his privilege but no question of fact or error is involved.

HENRY EYRING
W. F. K. WYNNE-JONES

Princeton University,
November 1, 1935.

Raman Spectrum of Acetylene

In a recent issue of the *Journal of Chemical Physics*, Glockler and Morrell[1] have reported six frequencies (382, 618, 631, 1762, 1959 and 3338) in the Raman spectrum of liquid acetylene and only two (1974 and 3374) in that of the gas. With a view to explain the larger number of frequencies in the former case, they have suggested that the acetylene molecule in the liquid may be regarded as nonlinear. In this connection, we wish to point out that a particularly intense Raman spectrum of acetylene gas has been obtained by us and the frequencies observed are 589, 646, 1973 and 3371. The spectrum can be quite satisfactorily explained in terms of Placzek's selection rules. 589 and 646 are the peaks of the unresolved P and R branches accompanying the Raman active δ oscillation at 614. The corresponding Q branch is missing as may be expected. 1973 and 3371 are the well-known Raman active valency oscillations. The corresponding frequencies in liquid acetylene may easily be recognized in the numbers given by Glockler and Morrell. Besides these, the above authors have evidently observed two Raman lines at 22,556 and 21,176 cm^{-1}, respectively, and have attributed them to λ4358. They thus obtain two new frequencies 382 and 1762. These lines have also been recorded by us in the gas and a casual examination of the picture is enough to show that they are merely the valency vibrations arising from the mercury line λ4077 which has a wave number 24,516. The two new lines of Glockler and Morrell will then give shifts of 1960 and 3340 which are in good agreement with their own values in the liquid state. There is no necessity of assuming a bent structure at all. The detailed interpretation of the Raman spectrum of acetylene is given by us in a paper which is to appear shortly in the *Proceedings of the Indian Academy of Sciences.*

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A. VEERABHADRA RAO

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Waltair (India),
February 19, 1936.

[1] Glockler and Morrell, J. Chem. Phys. **4**, 15 (1936).

The Formation of Hydrogen Peroxide in the Electrodeless Discharge in Water Vapor

Rodebush and Wahl[1] suggested that the formation of hydrogen peroxide in water vapor, which has been dissociated in the electrodeless discharge, might take place in part by a homogeneous bimolecular reaction. They pointed out that they had no direct evidence for this conclusion, but were inclined to the idea because of the conclusion of Bonhoeffer[2] that the hydroxyl radical had a very short life and also because the yield appeared to be independent of the length of time required for the hydroxyl to reach the liquid-air trap. Oldenberg[3] has since shown that Bonhoeffer's conclusion is incorrect, and has pointed out that the chief argument in favor of the homogeneous mechanism is, therefore, invalidated.

Recently the writers have been able to demonstrate that the reaction takes place entirely in the liquid-air trap, at least, under some conditions. When a trap cooled with a dry ice and acetone mixture is placed in front of the liquid-air trap, no hydrogen peroxide and, in some cases, very little water is condensed, although it is easily demonstrated that either substance, if present, would be condensed in the trap cooled with dry ice. The usual quantity of hydrogen peroxide and water is obtained in the liquid-air trap, regardless of whether the dry ice trap is interposed or not.

It is apparent that the dissociation of the water is more nearly complete than had been assumed. These results raise a number of questions which can only be answered by further investigation. It must be admitted that we still know very little about the chemical behavior of the hydroxyl radical.

R. W. CAMPBELL
W. H. RODEBUSH

Department of Chemistry,
University of Illinois,
Urbana, Illinois,
February 24, 1936.

[1] Rodebush and Wahl, J. Chem. Phys. **1**, 696 (1933).
[2] Bonhoeffer, Zeits. f. physik. Chemie **143**, 2 (1931).
[3] Oldenberg, J. Chem. Phys. **3**, 266 (1935).

Sucrose Inversion in H_2O-D_2O

Kinetic studies in H_2O-D_2O on the mutarotation of glucose,[1] the decomposition of nitramide[2] and the hydrogen ion catalyzed inversion of sucrose,[3, 4] for which the ratios k_{D_2O}/k_{H_2O} are about 1 : 3.8, 1 : 6, 2.1 : 1, respectively, show that the velocity constant $k_{H_2O-D_2O}$ does not vary linearly with the fraction of heavy water, $F_{D_2O}=\Delta s/0.1079$. The negative departure from linearity, which all exhibit, increases in the above order. Since $k_{H_2O-D_2O}$ probably depends only indirectly upon the medium it is important to consider other substances which may be present in isotopic modifications and kinetically significant.

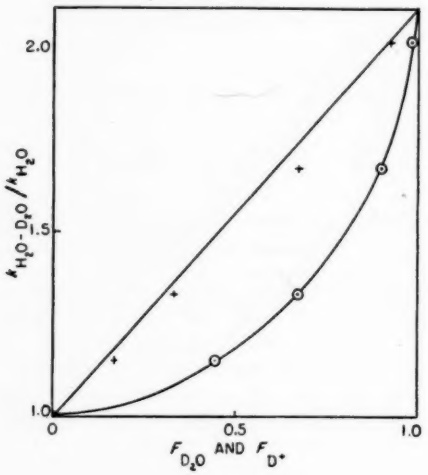

FIG. 1.

Since the inversion of sucrose in H_2O is catalyzed specifically by H^+ it seems likely that a simple relationship will exist between $k_{H_2O-D_2O}$ and the fraction of heavy hydrogen ion $F_{D^+}=(D^+)/(D^+)+(H^+)$. In Table I the first two columns give the data[3, 4] reported for this reaction and values of F_{D^+} in the third column are obtained from the equilibrium constant $K_1=15.7$[5] for the exchange reaction

$$H_2O+2D^+=D_2O+2H^+. \qquad (1)$$

It will be seen from the graph that a plot of $k_{H_2O-D_2O}/k_{H_2O}$ *vs.* F_{D^+} gives a nearly straight line (crosses), for an extrapolated value of 2.1 for k_{D_2O}/k_{H_2O}.

This is a specific application of a more general method which has already been applied to explain kinetic measurements on the mutarotation of glucose.[1] It may be applied to sucrose inversion without the necessity of identifying any substance, on the simple assumption that $k_{H_2O-D_2O}/k_{H_2O}$ varies linearly with the fraction $F_X=DX/HX+DX$ of some reactant or intermediate involved in the process of inversion. For each measured $k_{H_2O-D_2O}/k_{H_2O}$ there is an experimental F_{D_2O} and a corresponding F_X, which is obtained on the basis of the assumed linear dependence

$$F_X=[(k_{H_2O-D_2O})/k_{H_2O}-1]/1.1. \qquad (2)$$

For any F_{D_2O} the corresponding $R_w=(HDO)/(H_2O)$ is simply calculated, and $R_X=(HX)/(DX)=1-F_X/F_X$. Since $R_xR_w=K_x=K_3$ for the reaction

$$DX+H_2O=HX+HDO. \qquad (3)$$

Constancy of K_x values over the range H_2O-D_2O is a satisfactory test for the assumption made, as the last column of the table shows. Although it has been possible to identify K_x in the present instance with K_4 for the equilibrium (4)

$$D^+ + H_2O = H^+ + HDO, \quad K_4 = 7.2^{6} \qquad (4)$$

and in the previous example with the isotopic equilibrium constant for tetramethyl glucose, it can obviously be applied independently of any assumptions concerning the identity of HX and without foreknowledge of K_x. The method is not restricted to kinetic measurements.

TABLE I.

$\frac{\Delta s}{0.1079}$	$\frac{k_{H_2O-D_2O}}{k_{H_2O}}$	F_{D^+}	(H_2O)	(HDO)	$\frac{(HDO)}{(H_2O)}$	F_x	R_x	K_x
0.000	1.00	0.000						
0.444	1.15	0.169	17.84	25.92	1.45	0.14	6.2	8.9
0.671	1.33	0.332	6.57	23.32	3.54	0.30	2.3	8.3
0.90	1.67	0.677	0.65	9.78	15.0	0.61	0.64	9.6
0.981	2.01	0.921	0.025	2.10	84	0.92	0.087	7.3
1.000	(2.10)	1.000						

W. H. HAMILL

Fordham University,

V. K. LA MER

Columbia University,
March 14, 1936[7]

[1] Hamill and La Mer, J. Chem. Phys. **4**, 144 (1936).
[2] La Mer and Greenspan, unpublished measurements.
[3] Moelwyn-Hughes and Bonhoeffer, Naturwissenschaften **22**, 174 (1934).
[4] Gross, Suess and Steiner, ibid. **22**, 662 (1934).
[5] La Mer and Korman, preliminary measurements by E.M.F., unpublished.
[6] From (1) and $(HDO)^2/(D_2O)(H_2O) = 3.27$.

A New Comparison of the Viscosity of D_2O with that of H_2O

In an attempt to find a basis for comparison of the viscosity of D_2O with that of H_2O that might aid in explaining the observed difference,[1] it was noticed that at 15, 20, 25, 30 and 35°C, respectively, the viscosity of D_2O is almost the same as that of H_2O at a temperature 8.5° lower; or if $\eta_{H_2O}=f(T)$, then $\eta_{D_2O}=f(T-B)$ where f is the same function in both cases, and B is approximately 8.5°. This would explain the observed decrease in the ratio η_{D_2O}/η_{H_2O} with increasing temperature.[2] Several other physical properties of the two waters show somewhat analogous variations, e.g., the melting point of D_2O is 3.8°C,[3] and the temperature of maximum density for D_2O is 11.6°C,[4] 7.6° higher than that of H_2O.

The data are summarized in Table I. Column 1 gives the temperature, column 2 the viscosity of H_2O in millipoises,[5] column 3 the ratio η_{D_2O}/η_{H_2O},[2] and column 4 the viscosity

TABLE I. *The viscosity of D_2O compared with that of H_2O.*

T (°C)	η_1 Viscosity[1] of H_2O (millipoises)	$\frac{\eta_2}{\eta_1}$[2]	η_2 Viscosity of D_2O (mp)	η_1 compare with previous column	$\left(\frac{1}{\eta_1}\right)^{0.5}$ exp.	$\left(\frac{1}{\eta_1}\right)^{0.5}$[3] calc.	$\left(\frac{1}{\eta_2}\right)^{0.5}$ exp.	$\left(\frac{1}{\eta_2}\right)^{0.5}$[4] calc.
−4	20.5				7.0	7.0		
0	17.93[5]				7.47	7.52		
5	15.18[5]	1.309	19.88		8.11	8.13	7.09	7.09
				20.1				
10	13.09[7]	1.286	16.85		8.74	8.74	7.71	7.70
				17.02[5]				
15	11.44[7]	1.267	14.50		9.35	9.35	8.30	8.31
				14.50[4]				
20	10.08[7]	1.249	12.60		9.96	9.96	8.91	8.92
				12.56[0]				
25	8.94[9]	1.232	11.03		10.57	10.57	9.52	9.53
				11.01[4]				
30	8.00[4]	1.215	9.73		11.18	11.18	10.14	10.14
				9.72[4]				
35	7.20[8]	1.198	8.64		11.78	11.79	10.76	10.75
				8.64[8]				

[1] *International Critical Tables.*
[2] Lewis and MacDonald, J. Am. Chem. Soc. **55**, 4730 (1933).
[3] $(1/\eta_1)^{0.5}_{calc.}=0.122T+7.52$.
[4] $(1/\eta_2)^{0.5}_{calc.}=0.122T+6.48$.

of D_2O. In columns 4 and 5 the viscosity of D_2O at several temperatures is compared with that of H_2O at a temperature 8.5° lower. The agreement of the viscosity of D_2O at temperatures between 15° and 35° with the corresponding H_2O viscosity is very satisfactory. At the two lowest temperatures, 5° and 10°, respectively, D_2O has the same viscosity as H_2O at a temperature 8.2° lower.

To facilitate comparisons, $(1/\eta)^{0.5}$, which varies almost linearly with temperature, was plotted as a function of temperature. The values of $(1/\eta)^{0.5}$ for H_2O and D_2O, calculated from the experimental data are shown in columns 6 and 8, respectively. The values calculated from the equations $(1/\eta_1)^{0.5}_{calc.}=0.122T+7.52$, and $(1/\eta_2)^{0.5}_{calc.}=0.122(T-8.5)+7.52=0.122T+6.48$ are given in columns 7 and 9. These equations are purely empirical and do not hold at temperatures much above 35°C, but do show the relations $\eta_1=f(T)$ and $\eta_2=f(T-8.5)$ for the range 5° to 35°C.

WELDON N. BAKER

Allegheny College,
Meadville, Pennsylvania,
March 9, 1936.

[1] Most recent determination, $\eta_{D_2O}/\eta_{H_2O}=1.22996$ at 25°C, Jones and Fornwalt, J. Chem Phys. **4**, 30 (1936).
[2] Lewis and MacDonald, J. Am. Chem. Soc. **55**, 4730 (1933).
[3] La Mer and Baker, J. Am. Chem. Soc. **56**, 2641 (1934).
[4] Lewis and MacDonald, J. Am. Chem. Soc. **55**, 3057 (1933).
[5] *International Critical Tables.*